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CHARACTERIZATION AND DETERMINATION OF SURFACE BOUND HYDROGEN AND DEUTERIUM IN 1062, 4037 AND 4140 STEELS BY SECONDARY ION MASS SPECTROMETRY

FINAL REPORT

BY

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Executive Summary

Secondary Ion Mass Spectrometry (SIMS) is a technique that is sensitive to all elements, including hydrogen isotopes. The capability of the technique for measuring hydrogen concentrations in hydrogen charged steel surfaces has been assessed. The deuterium isotope was used in place of "light" mass-1 hydrogen* because of a high background from the latter isotope in most SIMS instruments. Deuterium surface concentrations were quantified using known concentrations of the deuterium isotope implanted into the steel samples being studied.

Surfaces of 1062, 4037 and 4010 steels were cathodically charged with deuterium and were analyzed by SIMS. Deuterium concentrations in the range of 1 - 8 atom percent were detected on the steel surfaces. Treatment of deuterium charged samples with Nitric, Acetic and Phosphoric (NAP) acid mixtures resulted in a significant decrease in the surface deuterium concentration. This was particularly so for 4037 steels where 90% of the deuterium was removed from the surface region by NAP treatment. Some efforts were also made to assess the effects of NAP treatment on the cathodically hydrogen charged steels.

Parallel experiments were done with the carrier gas technique for measuring bulk hydrogen concentrations. This technique showed that NAP treatment reduced the bulk hydrogen concentration in these specimens. Compared to the surface concentration of deuterium, the bulk concentration is less sensitive to NAP treatment.

Key Words: surface bound hydrogen, bulk hydrogen analyses, cathodic charging, Secondary Ion Mass Spectrometry, NAP treatment.

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* "light" mass-1 hydrogen is also known as protium

Sommaire Exécutif

La spectrométrie à masse des ions secondaires (SIMS) est une technique qui est sensible à tous les éléments incluant les isotopes de l'hydrogéne. Le pouvoir de rette technique pour mesurer la concentrention de l'hydrogéne introcluit à la surface des aciers a été évalué. L'isotope deuterium a été utilisé au lieu de l'hydrogéne 'légér' (masse = 1)* car la plupart des instruments SIMS ont un niveau résiduel d'hydrogéne résiduel assez élevé. La concentrention du deuterium à la surface a été déterminée en se basant sur des échantillons des mêmes aciers étudiés et qui ont été implantés avec des closes connues de deuterium.

Les surfaces des aciers types 1062, 4037 et 4010 ont été chargés cathodiquement avec du deuterium et ont été analysés avec le SIMS. Des concentrations de deuterium variant de 1 à 8 atomes pour cent ont été détectées dans la surface de ces aciers. Le traîtement des échantillons chargés de deuterium avec un mêlange d'acides Nitrique, Acétique et Phosphorique (solution NAP) a sensiblement réduit la concentration du deuterium à la surface. Cet effet est plus distingué dans le cas de l'acier type 4037 où 90% du deuterium a été enlevé de la surface par le traîtement avec la solution NAP. Quelques efforts ont été dépensées pour évaluer l'effet du traîtement avec la solution NAP sur les aciers qui ont été cathodiquement chargés avec l'hydrogéne.

Parallèlement à cette étude, des expériences ont été effectués pour déterminer la concentration totale de l'hydrogéne par la méthode basée sur l'entraînement dans un gaz. Ces expériences one démontré que le traîtement avec la solution NAP réduit la concentration totale de l'hydrogéne. L'effet de ce traîtement est moins prononcé sur la concentration totale que sur celle de la surface.

Mots Clés: hydrogéne lié à la surface, analyses de l'hydrogéne total, chargement cathodique, spectrométrie à masse des ion secondaires, traîtement avec la solution NAP.

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* l'hydrogéne 'léger' est aussi connu comme protium

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INTRODUCTION

1.1 General

The debilitating consequences of hydrogen interaction with metals are embrittlement, blistering and decarburization. Of these, the decarburization by hydrogen takes place at high temperatures (typically >700°C for steels) whereas hydrogen embrittlement and blistering take place at low temperatures. Embrittlement occurs under conditions where atomic hydrogen permeates the metal. This happens when the recombination of hydrogen atoms to form molecular hydrogen is inhibited, typically in the presence of poisons such as sulphide, cyanide, phosphorus and arsenic compounds. Such conditions often occur during cathodic protection, electroplating, etc.

1.2 Hydrogen Problems in Plated High Strength Steels

High strength low-alloy steels are often given corrosion protection by electroplating sacrificial coatings of cadmium or zinc. However, it is generally recognized that hydrogen introduced during pickling or plating diffuses to the areas of high stress and causes failure due to hydrogen embrittlement. Some of the hydrogen can be removed from the coating by baking (1). However, it has been shown that this additional step adds to the cost of the finished product (2,3) and that the removal of hydrogen after baking is rather incomplete (4). Hence, it is necessary to consider other pretreatment and post-treatment procedures that can effectively remove the surface hydrogen

before it permeates the steel. One such possibility, was investigated in the current context.

Two methods have been adopted for treating the surfaces of 1062, 4037 and 4340 high strength steels to permit the plating of cadmium, zinc and bismuth without embrittlement (5-7). In the first method, a smooth, clean, oxide-free surface is produced by pickling the steel with a mixture of Nitric, Acetic, and Phosphoric acids (NAP treatment). The second method consists of removing the oxide film, depositing a thin porous film of copper or zinc, and then treating with nitric-acetic acid mixture to remove the metallic film and produce a smooth surface devoid of minute sharp edges. Steel pins, subjected to these procedures were found to pass bend tests, showing that the hydrogen embrittlement had been minimized. The evaluation criterion in these bend tests was the success with which the pins could be bent through angles >135° without fracture. Based on this improvement, Rogers et al (5-7), hypothesized that the embrittlement originates in a thin layer existing at the surface of the metal. According to their hypothesis, when an embrittled test specimen is bent or stretched, a crack develops in this layer and spreads through the specimen resulting in fracture. This seemed to be a reasonable explanation since embrittlement can be eliminated by NAP treatment.

1.3 Estimation of Hydrogen Levels in Steels

Bend tests or any other tensile tests provide useful diagnostic data which correlate qualitatively with variations in hydrogen embrittlement susceptibility that can be related to bulk hydrogen levels in steels. However, it is still important to assess the surface hydrogen concentrations to derive a quantitative relationship between hydrogen embrittlement and hydrogen concentration. In this context, Sastri et al (8) measured hydrogen contents of 1062 and 4037 steels which had been heat treated to hardnesses in 51-56 HRC range, and then treated with NAP. The hydrogen content was analyzed by the carrier gas extraction procedure, which measures the total hydrogen present in the specimen. It was shown that NAP treatment removed 70% and 52% hydrogen from 4037 and 1062 steels, respectively, based on total sample weight.

The measured concentration of hydrogen (8) in an uncharged bulk steel specimen was in the range 0.5-2 μg/g (30-120 ppm atomic). Since hydrogen is believed to accumulate mainly in the surface layers, the surface concentrations of a hydrogenated specimen could be orders of magnitude higher than that measured as a bulk concentration. It is thus essential to determine hydrogen concentrations at the surface as well as at various depths in the bulk of steel. This can be accomplished by means of a suitable surface analytical technique, such as Secondary Ion Mass Spectrometry (SIMS).

1.4 Secondary Ion Mass Spectrometry for Analysis of Hydrogen in Steels

Some surface spectroscopic techniques that are being used to analyze hydrogen in metals include: Nuclear Reaction Analysis (10), and Secondary Ion Mass Spectrometry (SIMS). For the present study, SIMS was chosen because of its sensitivity and the rapidity in measuring concentration profiles. In SIMS, specimens are bombarded with a beam of primary ions (1-20 keV) causing the outermost layers to be sputtered away. Most of the sputtered fragments leave as neutral species, but a small fraction leaves either as positive or negative ions. These ions are then focused into a mass spectrometer and analysed according to their mass to charge ratios. Since the primary ion beam continuously erodes the sample surface, the measurement of one or several masses as a function of time yields an in-depth concentration profile. The mass spectrometer is capable of identifying all elements in the periodic table, complete with isotopic information, and this enables SIMS to distinguish between usual mass-1 hydrogen* and its isotopes deuterium and tritium (11). By means of this technique, it has been possible to detect hydrogen and carbon in silicon (11), aluminum and magnesium alloys (12), nickel (13) and beryllium (14). There is no evidence to date of any previous depth profiling work of hydrogen in steels and stainless steels. However, SIMS has previously been used to measure the lateral distribution of hydrogen in welded portions of carbon steel (15) and stainless steel (16). In view of the applicability of

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* Mass-1 hydrogen is also known as protium

SIMS to other metal- and metalloid-hydrogen systems, it was felt that there is adequate justification for applying this technique to characterize the surface-bound hydrogen in high strength steels.

Since it was shown that NAP treatment minimized hydrogen embrittlement in 1062 and 4037 steels, these steels were chosen for study in this program. Hydrogen (protium)- as well as deuterium-charged steels, with and without NAP treatment were analyzed by SIMS. Deuterium-charged steels were investigated so that the high hydrogen background emanating from any surface containing adsorbed water could be avoided. The SIMS study was extended to include deuterium-charged AISI type 4140 steel. This steel is used in high strength machine parts, such as connecting rods, crankshafts and drill bits.

In this report, we present the results of SIMS analyses of hydrogen- and deuterium-charged 1062, 4037 and 4140 steels and the results of NAP treatments, as well as some comparisons with the complementary data obtained by the carrier gas thermal conductivity technique.

OBJECTIVE

To evaluate the reasons for the improvement in hydrogen embrittlement resistance of certain steels (AISI 1062, 4037 and 4140) by monitoring surface-bound hydrogen/deuterium concentration before and after pickling treatment, by Secondary Ion Mass Spectrometry (SIMS).

EXPERIMENTAL

3.1 Materials - Chemical Composition, Heat Treatment, Metallography and Hardness Measurements

AISI 1062, 4037 and 4140 steels were selected for hydrogen and deuterium charging and subsequent bulk analyses by hot extraction carrier gas technique and surface characterization by SIMS. The first two grades of steels were obtained from CANMET/PMRL in the form of flattened nails (thickness 3 mm; width 4 mm; length 80 mm). AISI type 4140 steel was available as 32 mm diameter bar stock. The chemical compositions of these steels are shown in Table 1.

The AISI 1062 and 4037 steels were already heat treated prior to flattening. The heat treatments for these two grades of steels were as follows:

i) AISI 1062 - austempered* in bainitic range to an expected hardness of 52-56 HRC. The material is covered with thin bluish oxide scale.

ii) AISI 4037 - quenched** and tempered to a hardness of 51-55 HRC.

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* Quenched in a molten salt bath maintained at somewhat above the M_s (initiation temperature for martensite formation) temperature, i.e. 274°C. This is done in order to avoid quench cracking.

** Oil quenched from 845°C; tempered at 205°C

The hardness of AISI 4140 steel prior to heat treatment was 16 HRC. This steel was also subjected to quench-tempering treatment*** so as to give hardnesses within 51-56 HRC (same as for 1062 and 4037 steels). Hardness of the steels was measured after polishing and the as-measured hardnesses were in 47.5 - 51.0 HRC range. The microstructures of these steels shown in Figure 1, correspond to those of low temperature transformation products.

3.2 Cathodic Hydrogen/Deuterium Charging Procedure

Before charging, the AISI 1062, 4037 and 4140 steel samples (sizes - 1062 and 4037 steels: 19 x 3 x 4 mm; 4140 steel: 10 x 2 x 2 mm) were polished on wet SiC papers (240, 320, 400 and 600 grit) and ulstrasonically cleaned in acetone. Then they were cathodically polarized in 1N sulphuric acid solutions containing 2 g/ℓ arsenous trioxide (As_2O_3). Arsenous trioxide was used as hydrogen recombination poison to increase hydrogen uptake by the steels. For deuterium charging, deuterated solutions, i.e. deuterated sulphuric acid - D_2SO_4 dissolved in D_2O, containing 2 g/ℓ of As_2O_3 were used. An inert atmosphere was maintained by bubbling nitrogen throughout the charging. During the first one hour prior to the sample immersion, nitrogen was bubbled into the solution by placing the nitrogen inlet tube inside the solution. After sample immersion and while charging, the N_2 was bubbled above the solution by placing the

*** Oil quenching from 845°C; tempered at 260°C.

nitrogen inlet tube above the solution inside the cell. The charging was done at 50 mA for 20h. The charged samples were washed in distilled water, methanol and stored in liquid nitrogen until analyzed. Another group of samples was prepared by treating the charged steels in NAP solution, of composition: conc. HNO_3 - 23 ml, conc. H_3PO_4 - 25 ml, glacial acetic acid - 23 ml diluted to 100 ml with distilled water. The NAP pickling treatment times were 1 min. for 1062 and 3 min. for 4037 and 4140 steels. These times were established on the basis of preliminary hydrogen charging, pickling and bulk hydrogen analyses by carrier gas-thermal conductivity bridge procedure. Alternatively, some hydrogen charging attempts were made by exposing 1062 steel samples to "NACE" solution*. This solution composition was: 5% NaCl, 0.5% glacial acetic acid, H_2S saturated at room temperature after N_2 presaturation. After 96h exposure, it was found that hydrogen levels in the steel were nearly the same as those obtained by cathodic charging. For this reason, only cathodic charging was used throughout this program.

3.3 Bulk Hydrogen Analyses by Carrier Gas Procedure

Bulk hydrogen analyses were carried out with an intent of establishing the surface hydrogen uptake during cathodic charging and the permissible time limit within which SIMS analyses should be carried out and finally the extent to

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* This solution is usually used for testing steels or stainless steels for hydrogen sulphide cracking according to "NACE" (National Association of Corrrosion Engineers) standard TM-01-77.

which NAP treatment removes the charged hydrogen. Some samples were also included to analyze the residual hydrogen levels in uncharged steels. Usually a minimum of three samples were used for a given condition, and an average of three values or best two out of three values are reported.

The bulk hydrogen content of the steel samples was determined by carrier gas procedure using a Leybold-Heraeus hydrogen determinator, Model H2A 2002, with an approximate detection limit of 0.1 ppm and a resolution of ±0.01 ppm (by weight). The instrument measures the thermal conductivity of hydrogen liberated from samples in a stream of high-purity nitrogen at 1100°C (hot extraction method). Standard steel balls obtained from Alpha Resources (Stevensville, MI) were used for calibrating the hydrogen analyzer (9).

3.4 Hydrogen Determination by Secondary Ion Mass Spectrometry

Secondary Ion Mass Spectrometry involves the mass measurement of charged particles removed from the top 1-2 monolayers of a surface by a primary ion beam. The resultant mass spectrum indicates the chemical elements which are present on this surface. The primary ion beam gradually penetrates the material by the sputtering process. Thus, a change in mass spectral composition with time can be related to a change in material composition as the surface is probed to increased depths. This is called a depth profile, and it is used in this work to measure the change in hydrogen concentration with depth into the oxide layer.

Mass spectral measurements enjoy relative freedom from the background noise compared to most other spectroscopies. Thus, it is possible to measure, at adjacent mass numbers, intensities differing by a factor of 10^5. From this large dynamic range comes the high elemental sensitivity for which SIMS is so well known.

The measurement of masses also has another advantage. Different isotopes of the same element can be readily distinguished and, if desired, the element can be "tagged" by enrichment of one particular isotope. Such a "tagged" element is more easily distinguished above a background caused by spurious sources of the same element. This is the case for hydrogen in most SIMS measurements. While hydrogen can be readily distinguished in many SIMS experiments, most of the hydrogen originates from water molecules in the spectrometer itself, and this background can mask any hydrogen released from a hydrogen charged metal surface. The availability of the deuterium isotope ($m/_e = 2$) obviates the background problem and thus enhances the working sensitivity.

The SIMS measurements were made in a Cameca IMS-3F ion microscope using a primary beam of Cs^+ (500-1200 nA current and 10 keV accelerating voltage). Cesium is used to enhance the sensitivity of electronegative elements such as hydrogen, and negative secondary ions are usually collected. Typically, $^1H^-$, $^2D^-$, $^{56}Fe^-$, $^{75}SiO_2^-$ and $^{75}As^-$ were collected as a function of time until it was clear that the primary beam had penetrated well past the oxide layer on the specimen, and into the underlying metal. Such a depth profile usually penetrated to a depth of 5-10 μm, and this required approximately 10-60 minutes of time.

The conversion of SIMS intensities to elemental concentrations is not straightforward. There exists no universal calibration coefficient since SIMS yields can be strongly altered by the matrix. Therefore, for most quantitative work, it is advisable to prepare reference standards using the same analytes and matrices under investigation. This is best accomplished by "doping" a known quantity of an element into the matrix and then measuring the total ion signal obtained for the "dopant" during a depth profile. The doping procedure is almost always accomplished by ion implantation, i.e. by accelerating a high energy ion beam into a material so that all of the element is distributed within the top few microns of the surface.

For the case of deuterium detection, a beam of 15 keV D_2^+ was implanted into polished (0.25 μm roughness) surfaces of 4037 and 1062 nails using the low energy mass separator at Chalk River Nuclear Laboratories. Ion doses of 1×10^{14} atoms/cm^2, 5×10^{14} atoms/cm^2 and 1×10^{15} atoms/cm^2 were implanted in each type of specimen. Immediately following each implantation, the specimen was immersed in liquid nitrogen, where it remained until ready for SIMS analysis. Storage at cryogenic temperatures until analysis was felt sufficient to reduce to a negligible minimum loss of deuterium by diffusion. Such a view was vindicated by the measurement of identical deuterium depth profiles on the same specimen on two separate occasions separated by 7 days. On the second occasion, the specimen had already been previously removed from its cryogenic surroundings for some 45 minutes. An implanted specimen deliberately left at room temperature for 24 hours exhibited a deuterium loss of ~50%.

In a procedure that will be described later, the SIMS profiles obtained with ion-implanted steels were used for quantitative analyses of deuterium in deuterium-charged steels with and without the NAP treatment.

Initially, three locations on each unknown surface were analyzed. However it became evident that there was insignificant variation between areas. The distribution of H^- on a microscopic scale could be measured by the imaging capability of the spectrometer. However, no localized variations could be detected in such images to a resolution of <25 μm. Subsequently, only one analysis per specimen was made and the total number of specimens was correspondingly increased to three samples per each surface conditioning treatment.

RESULTS AND DISCUSSION

4.1 Bulk Hydrogen in AISI 1062, 4037 and 4140 Steels: Results of Hydrogen Analyses by Carrier Gas Technique

The bulk hydrogen concentrations in AISI 1062, 4037 and 4140 steels, as estimated by carrier gas procedure, are shown in Table 2. The hydrogen levels in heat-treated, polished, uncharged steels were 1.2 ±0.1, 1.7 ±0.2 and 0.6 ±0.06 μg/g (average of five measurements) for AISI 1062, 4037 and 4140 grades, respectively. Cathodic charging increased the corresponding bulk hydrogen levels from the above values to 15 ±0.4, 22 ±3.8 and 13 ±1 μg/g (0.08, 0.13 and 0.07 atomic percent hydrogen, respectively). Exposures of charged 1062, 4037 and 4140 steel specimens to air at room temperature for 30 min, resulted in 18, 40 and 32 percent hydrogen losses to the atmosphere. Even though the SIMS depth profiles were acquired for periods slightly exceeding 30 mins up to a maximum of 40 minutes, useful inferences from these profiles were drawn from the very early part of these profiles corresponding to first 10 min (10 min = approximately 5 μm thick sputtered layer) where the hydrogen losses to the atmosphere can be well below the above reported hydrogen loss data.

The previously demonstrated (8) beneficial influence of NAP treatment in removing bulk hydrogen from these charged and uncharged steels is shown in Table 3. NAP treatment removed 52 and 70 percent of bulk hydrogen from heat-treated 1062 and 4037 steels that were overlayed with either blue oxide (1062 grade) or copper deposits (8). On the other hand, in this work, NAP treatment removed 35, 65 and 44 percent of bulk cathodically charged hydrogen from AISI 1062, 4037 and 4140 steels, respectively.

4.2 SIMS Analyses

4.2.1 Pickled 1062 and 4037 Steels (No Deuterium Isotope Injected)

Since NAP treatment lowered the hydrogen levels in as-received steels, as discussed previously, it was felt that SIMS analyses on pickled steels under this condition might provide baseline data for comparison of the data under hydrogen and deuterium-charged conditions with and without NAP treatment. In addition, some of the steels, were treated separately, first with hydrochloric acid, then with nitric and acetic acid mixture, and were subsequently subjected to SIMS analyses. The conditions under which these two steels were acid treated are listed below:

Steel	Solution
4037	50 ml conc HCl + 50 ml water
1062	23 ml conc HNO_3 + 23 ml glacial acetic acid + 54 ml water
4037	23 ml conc HNO_3 + 23 ml glacial acetic acid + 54 ml water
1062	NAP solution - 23 ml conc HNO_3 + 23 ml glacial acetic acid + 25 ml phosphoric acid + 29 ml water
4037	NAP solution - 23 ml conc HNO_3 + 23 ml glacial acetic acid + 25 ml phosphoric acid + 29 ml water

The treatment time was 1 minute.

The SIMS depth profiles for iron 56, hydrogen 1, deuterium 2 and copper 63 are shown in Appendix I. The profile of mass 75, initially thought to be due to arsenic-related species, is questionable because arsenic

related species are deposited only during cathodic charging in acid solutions containing arsenous trioxide as cathodic poison. It is possible that the species detected is the molecular ion SiO_2^-, corresponding to the silicon present in these steels. The time of sputtering in these depth profiles, for each mass, is proportional to the sputtered depth. The initial and final signal intensities for iron, hydrogen, deuterium and copper are listed in Table 1 of this Appendix I. From the signal intensity values in this table, it was possible to calculate the initial and final signal ratios for $^1H^-/^{56}Fe^-$, $^2D^-/^{56}Fe^-$, and $^{63}Cu^-/^{56}Fe^-$. These ratios are shown in Table 4, and from this table, it can be seen that the initial $^1H^-/^{56}Fe^-$ ratios are 10^4 times greater than $^2D^-/^{56}Fe^-$ ratios and the final $^1H^-/^{56}Fe^-$ ratios are 100 times greater than $^2D^-/^{56}Fe^-$ ratios. The surface deuterium concentrations were determined from $^2D^-/^{56}Fe^-$ using the calibration implant data, and these concentrations were found to be in the range 0.1 - 1 μg/g (0.005 - 0.05% atomic). The procedure that was used for surface deuterium calculation is described in section 4.2.3 - deuterium-charged AISI 1062, 4037 and 4140 steels. While the data based on deuterium uptake can be regarded as quantitative, the hydrogen-based measurements are qualitative. They are affected by the background from water adsorbed on the surface.

4.2.2 Hydrogen (Protium Isotope)-Charged AISI 1062 and 4037 Steels

The SIMS depth profiles of protium isotope-charged AISI 1062 and 4037 steels before and after NAP treatment are shown in the Figures of

Appendix II. In this case, profiles with mass 75 could be assigned also to the arsenic species visually observed on the surface as well as the SiO_2^- species. The initial and final secondary ion signal intensities of iron, hydrogen, deuterium and copper are tabulated in Table 1 of Appendix II, and the $^1H^-/^{56}Fe^-$ and $^{63}Cu^-/^{56}Fe^-$ signal intensity ratios are shown in Table 5. The $^2D^-/^{56}Fe^-$ ratios are not calculated here since an examination of the signal intensity data in Table 1 - Appendix II shows that the ratios are in the same range as those in Table 5. Thus, even in hydrogen-charged steels, the background deuterium levels are comparable to those in pickled steels. However, a comparison of data in Tables 4 and 5 for pickled and hydrogen charged steels reveals that:

i) the initial $^1H^-/^{56}Fe^-$ ratios for the charged 1062 steels (Table 5) are greater than those for the nitric-acetic acid or NAP treated uncharged 1062 steels (Table 4);

ii) the initial $^1H^-/^{56}Fe^-$ signal ratios are lowered for 1062 steels when the charged steels are NAP-treated (Table 5);

iii) for 4037 steels, the influence of NAP treatment in $^1H^-/^{56}Fe^-$ ratios are rather mixed (Table 5);

iv) there is an enhancement of the $^{63}Cu^-/^{56}Fe^-$ signal ratio after NAP treatment (Table 5).

The trends in signal ratios, as described here for example, could be considered to qualitatively indicate the relative variations in surface concentrations. Thus, based on $^1H^-/^{56}Fe^-$ signal ratio variations it can be generalized that for 1062 steel there is an increase in surface hydrogen concentration upon cathodic hydrogen charging corresponding to

the increments in signal ratios (see item i, above), and a decrease in surface hydrogen concentrations upon NAP-treatment. Some mixed effects that were noted for 4037 steels, (item iii above) can be attributed to the erratic changes resulting from background hydrogen that could be present in the SIMS system. The symptoms of copper enrichment after the NAP-treatment of the hydrogen-charged steels are indicated in the increases of $^{63}Cu^-/^{56}Fe^-$ signal ratios upon NAP treatment.

4.2.3 Deuterium-Charged 1062, 4037 and 4140 Steels

Signals and Signal Ratios

A typical SIMS spectrum of a deuterium charged surface of 4037 steel is shown in Figure 2. This spectrum shows the usual presence of hydrogen, deuterium, carbon, sulphur and even dilute constituents such as chromium (re: Table 1). The actual SIMS depth profiles of deuterium charged 1062, 4037 and 4140 steels before and after the NAP treatment are shown in the figures of Appendix III. The initial and final secondary ion signal intensities are tabulated in Table 1 of Appendix III. The signal intensity ratios are presented in Table 6. The key intent was to establish if deuterium uptake due to charging and the consequences of NAP treatment could be diagnosed by SIMS. It is clear from the table that there is major enhancement in the $^2D^-/^{56}Fe^-$ signal ratio upon cathodic charging (cf. Table 4) due to deuterium uptake by these steels. Also, the $^2D^-/^{56}Fe^-$ ratios clearly decrease as a result of NAP treatment.

Calculation of Deuterium Concentrations from Signal Ratios

The signal ratio data were used to further calculate the atomic concentrations by making use of calibration values obtained from the SIMS depth profiles of deuterium isotope-implanted 1062 and 4037 steels. The procedure for these calculations and acquisition of deuterium concentration vs depth profiles is described below.

As a first step in these calculations, the ion intensity vs sputtered depth profiles were collected for the D_2^+ ion-implanted 1062 and 4037 steels. A typical ion intensity (c/s) vs sputtered depth (μm) profile of 4037 steel that is monoatomic ion-implanted with a dose of 1×10^{15} at/cm^2 of 30 keV D_2^+ ion is shown in Figure 3. In this figure it can be seen that the range peak is very close to the outer surface. The implant profiles were quantified by equating the integrated signal in counts/s to the known dose, and the implant profile could then be replotted in terms of concentration, refer to Figure 4, for example. By referencing a particular point on the curve to the $^{56}Fe^-$ signal, a calibration constant for the matrix was obtained. The same calibration constant was obtained for 1062 and 4037 steels. This could then be used to plot the concentration of deuterium on an unknown steel surface. In all cases, the ion beam crater depth was measured by a Dek-tak IIA profilometer after the profile. This was used to plot the real depth of a profile in Figures 3 and 4 rather than a sputtering time.

The deuterium isotope depth profiles, i.e. deuterium concentration (atoms/cm^3) vs sputtered depth plots for 1062, 4037 and 4140 steels are

shown in Appendix IV. The calibration SIMS profiles for 4140 steels were not obtained and therefore the deuterium concentrations in 4140 steels were calculated from the available calibration data for implanted 4037 steels. Some typical profiles, illustrative of the beneficial effects of NAP treatment in removing deuterium from the charged 1062, 4037 and 4140 steels are shown in Figures 5, 6 and 7, respectively. Actual deuterium isotope concentrations as well as percent deuterium isotope removed upon NAP treatment as well as bulk hydrogen that is removed due to NAP (for comparison) are shown in Table 7. In this table it can be noted that the surface bound deuterium concentration is highest in 4037 and lowest in 4140 steels. The NAP treatment removes the surface bound deuterium by 53% in 1062, 90% in 4037 and 40% in 4140 steels. If these values are considered to represent the mass-1 hydrogen indirectly, then a comparison with the bulk H_2 that is removed due to NAP shows that higher concentrations are removed from the surface than from the bulk of 1062 and 4037 steels.

At this point, it must be emphasized that the assessments of NAP treatment effects are based on SIMS profiling of the individual specimens of charged steels (one charged steel sample) with and without NAP treatment rather than SIMS profiling the same specimen before and after NAP. Therefore, the observation that there were no differences between the extents to which D_2 (or H_2) have been removed from the surface and bulk of 4140 steel (re: Table 7) merits a careful consideration and further work.

For deuterium-charged 1062 steel, the deuterium concentration is 6 x 10^{21} at/cm^3. Since the concentration of iron itself is 8.6 x 10^{22} at/cm^3 the relative deuterium concentration is 7.0% atomic or 2200 μg/g. This is about 100 fold higher than the concentration of hydrogen in a charged 1062 specimen as determined by carrier gas technique!. This latter technique gives a much lower concentration because the hydrogen measured is based on the mass of the whole specimen rather than just the surface region affected.

The effects of NAP treatment appear more clearly when measured by changes in surface deuterium. The observed differences between NAP treatment effects on surface deuterium concentration and bulk hydrogen concentration may be accounted for on the basis of surface segregation of silicon, chromium, nickel and molybdenum in these steels. The total concentration of these elements is maximum in AISI 4140 steel, hence the percentage deuterium removed by NAP treatment may be lowest. This explanation is rather speculative and requires additional work.

During the SIMS analysis of these steels for deuterium concentration, the microscopic capabilities of the instrument were used in an attempt to see if there was any lateral variation in the surface deuterium concentration. It was reasoned that the selective hydriding of segregated silicon, chromium, nickel and molybdenum might be observable. Therefore, initial attempts were made by imaging different locations D_2^+ ion implanted 4037 steel for deuterium. No differences could be found possibly due to a lack of dilineation in grain boundaries in this grade of steel under flattened (by rolling) and quench-tempered condition.

As was reported previously for hydrogen charged steels, NAP treatment of deuterium charged steels caused enrichment of copper on the steel surfaces. This is seen in Table 6 where the $^{63}Cu^-/^{56}Fe^-$ ratio is compared for charged and pickled specimens (re: Tables 4 and 5).

This work has shown that SIMS can be used quantitatively to detect hydrogen isotopes on steel surfaces. This is the first known report of such a measurement. The work has also shown that NAP treatment of a hydrogen-charged surfaces does result in the removal of significant quantities of hydrogen from the surface itself. The absolute concentration of hydrogen detected in the surface layer is much higher than is detected in the bulk of the sample by the carrier gas technique. This can be ascribed to the very large volume sampled by carrier gas technique, most of which contains little hydrogen. Since most hydrogen is concentrated at the surface, the SIMS technique gives a localized and more accurate determination of hydrogen concentration as deuterium.

4.3 Proposed Future Studies

Despite these advances there is much that could be done to improve the use of SIMS for the study of hydrogen in metals. Firstly, there is a memory effect in the instrument which causes an unacceptably large persistance in the deuterium signal as the surface layer is penetrated. After the surface has been sputtered for 2 minutes it is difficult to separate the "real" and memory components of the signal. This memory effect is caused by deuterated water and other species which are not pumped rapidly enough from the sample region. We

would propose the use of double deuterium implants - one shallow and the other deep, to assess the present memory effect. Surface Science Western is presently designing a cryogenic mini-shield which would almost entirely surround the sample at 15° - 20°K. This type of system will be important if extensive studies of hydrogen distribution as a function of depth were contemplated.

In this program only NAP treatment of hydrogen-charged steels has been investigated. The high sensitivity to the deuterium isotope should allow the treatment by individual acids to be explored, as well as the effect of active thin film coatings on the steel surface. In the present study, the aspect of deuterium segregation at preferred sites has not been understood. An extension to this program would be to study the deuterium segregation in 4140 steel, a widely used steel. These samples are already available in heat-treated condition. The polished samples of this steel can be reheat-treated to a larger grain size and then be implanted with deuterium at various known dosages and then examined under SIMS by depth profiling at matrix, grain boundary and precipitates of this steel. If segregation effects are considered as precursors to embrittlement it is then hoped that this type of surface studies will further our understanding of hydrogen interactions with preferred sites in metal. In addition to this, one could also consider evaluting the surface distribution of H_2 as well as degradation products of metal by H_2S in metal - H_2S systems by using labelled D_2S for convenience of examination. A similar approach may be extended to study H_2 phenomena in welds and weld overlays. Thus, it is hoped that the present study has served as a small step toward continued utilization of SIMS technique in further studying other related metal-hydrogen systems.

CONCLUSIONS

5.1 Bulk Hydrogen Analyses

1. Bulk hydrogen concentrations in AISI 1062, 4037 and 4140 steels were analyzed by carrier gas technique. It was found that the residual bulk hydrogen levels were in 0.6 - 1.7 μg/g range and were increased to 12 - 23 μg/g upon cathodic hydrogen charging.

2. From bulk hydrogen analyses, it was established that NAP treatment of charged steels removed bulk hydrogen as follows:

Steel	% H_2 Removed
1062	35
4037	65
4140	44

5.2 SIMS Analyses

1. SIMS depth profiles were obtained for deuterium-charged 1062, 4037 and 4140 steels with and without NAP-acid treatment. There were large enhancements in $^{2}D^{-}/^{56}Fe^{-}$ signal ratios when compared to as-pickled or hydrogen (protium isotope)-charged steels, thereby indicating deuterium isotope uptake during cathodic deuterium charging.

2. The calibration data obtained from D_2^+ ion-implanted 1062 and 4037 steels were used to convert the $^2D^-/^{56}Fe^-$ signal ratios into atomic concentrations and to generate atomic concentration vs sputtered depth profiles and assess the NAP-treatment effects.

3. By this procedure it was found that the NAP acid treatments removed the surface deuterium from the deuterium charged steels as follows:

Steel	% Surface D_2-Removed by NAP-Treatment
1062	53
4037	90
4140	40

4. SIMS depth profiles were obtained for 1062 and 4037 steels in pickled and as hydrogen-charged conditions with and without NAP treatment. The hydrogen depth profiles indicated of substantial background hydrogen even in pickled steels that were supposed to contain traces of hydrogen. The deuterium signals and $^2D^-/^{56}Fe^-$ signal ratios were at least 100 - 10,000 times lower than $^1H^-/^{56}Fe^-$ signal ratios, thereby indicating that the deuterium isotope levels in SIMS analytical equipment are negligible.

5. Copper depth profiles of variously NAP-treated steels showed that NAP treatment caused copper enhancement on the steel surfaces upon NAP treatment. This assessment was based on comparisons of $^{63}Cu^-/^{56}Fe^-$ signal ratios of as-charged and NAP-treated steels.

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TABLE 1

CHEMICAL COMPOSITIONS OF AISI 1062, 4037 and 4140 STEELS (%W/W)

Steel	C	Mn	Si	P	S	Cr	Ni	Mo	Cu
1062	0.64	1.04	0.20	0.01	0.03	0.06	0.01	--	0.07
4037	0.44	0.73	0.27	0.01	0.03	0.06	0.03	0.24	0.05
4140	0.43	1.21	0.38	0.01	0.02	0.93	0.28	0.10	N/A

N/A - not analyzed

TABLE 2

HYDROGEN CONCENTRATIONS IN AISI 1062, 4037 AND 4140 STEELS

Hydrogen was determined by thermal conductivity procedure. Hydrogen concentrations are expressed in μg/g (p.p.m.). Charging under cathodic conditions: 1N H_2SO_4 + 2 g/ℓ As_2O_3 solutions at room temperature. Current = 50 mA, time = 20h.

Steel	Condition	Average* Hydrogen Concentration μg/g
1062	Uncharged	1.2 ±0.1
4037	Uncharged	1.7 ±0.2
4140	Uncharged	0.6 ±0.06
1062	Charged	15.0 ±0.4
1062	Exposed to NACE solution**	17.3 ±1.5
1062	Charged - 0.5h room temperature	12.7 ±1.7
1062	Charged - 1.0h room temperature	15.3 ±1.2
1062	Charged - NAP treated (1 min)	9.7 ±0.1
4037	Charged	22.2 ±3.8
4037	Charged - 0.5h room temperature	13.2 ±2.5
4037	Charged - 1.0h room temperature	14.3 ±2.0
4037	Charged - 2.0h room temperature	12.0 (one meas.)
4037	Charged - NAP treated (2 min)	13.5 ±1.5
4037	Charged - NAP treated (3 min)	7.8 ±0.4
4140	Charged	12.6 ±1.0
4140	Charged - 0.5h room temperature	8.1 ±0.4
4140	Charged - 1.0h room temperature	7.5 ±0.4
4140	Charged - NAP treated (3 min)	7.1 ±0.1

* Number of measurements: uncharged steels - 5
charged steels - 3

** Exposure time - 96h

NAP is a mixture of Nitric, Acetic and Phosphoric acids. Composition: conc. HNO_3 23 ml, conc. H_3PO_4 25 ml, glacial acetic acid diluted to 100 ml with distilled water

TABLE 3

EFFECT OF NAP TREATMENT ON HYDROGEN REMOVAL - FROM THERMAL CONDUCTIVITY DATA

Steel	Condition	% Hydrogen Removed by NAP Treatment	Remarks
1062	As-heat treated	52[1]	After V.S. Sastri et al (8)
4037	As-heat treated	70[2]	After V.S. Sastri et al (8)
1062	Charged	35	Present work
4037	Charged	65	Present work
4140	Charged	44	Present work

[1] Covered with bluish oxide layer after heat-treatment

[2] Covered with copper film after heat-treatment

TABLE 4

SECONDARY ION INTENSITY (SIGNAL) RATIOS FOR PICKLED AISI 1062 AND 4037 STEELS

Steel	Condition	Signal Ratio[1] $^{1}H^{-}/^{56}Fe^{-}$ I	$^{1}H^{-}/^{56}Fe^{-}$ F	$^{2}D^{-}/^{56}Fe^{-}$ I	$^{2}D^{-}/^{56}Fe^{-}$ F	$^{63}Cu^{-}/^{56}Fe^{-}$ I	$^{63}Cu^{-}/^{56}Fe^{-}$ F
4037	50% HCl						
	Location 1	0.7	0.05	0.0006	0.0006	7.4	1.1
	Location 2	1.1	0.08	0.0008	0.0002	8.1	0.04
	Location 3	1.3	0.04	0.0010	0.0005	---	--
1062	Nitric + Acetic Acid						
	Location 1	0.2	0.05	0.0003	0.0001	1.9	0.03
	Location 2	0.5	0.03	0.0050	<0.0001	---	--
	Location 3	0.3	0.02	0.0001	<0.0001	---	--
	Location 4	0.7	0.02	0.0003	<0.0001	---	--
4037	Nitric + Acetic Acid						
	Location 1	1.8	0.07	0.0003	<0.0001	---	--
	Location 2	1.8	0.30	0.0008	0.0001	---	--
1062	Nitric + Acetic + Phosphoric Acid - NAP						
	Location 1	1.4	0.09	0.0003	<0.0001	5.0	0.06
	Location 2	2.1	0.07	0.0006	<0.0001	---	--
4037	Nitric + Acetic + Phosphoric Acid - NAP	1.5	0.07	0.0004	<0.0001	---	--

[1]The initial (I) and final (F) signal ratios, as shown under each column are calculated from the data in Table 1 of Appendix I.

TABLE 5

SECONDARY ION INTENSITY (SIGNAL) RATIOS FOR HYDROGEN CHARGED AISI 1062 AND 4037 STEELS

Steel	Condition	Signal Ratio[1] $^{1}H^{-}/^{56}Fe^{-}$ I	$^{1}H^{-}/^{56}Fe^{-}$ F	$^{63}Cu^{-}/^{56}Fe^{-}$ I	$^{63}Cu^{-}/^{56}Fe^{-}$ F
1062	Charged				
	Sample 1	3.2	3.0	1.6	8.60
	Sample 2	6.5	5.9	---	--
	Sample 3	3.1	1.3	6.1	0.10
	Sample 4	2.2	0.9	8.2	0.03
1062	Charged + NAP Treated - 1 min				
	Sample 1	0.8	4.6	93.1	0.1
	Sample 2	1.4	2.3	--	---
	Sample 3	1.1	3.3	32.9	0.2
	Sample 4	1.7	1.0	53.3	0.3
4037	Charged				
	Sample 1	0.7	1.4	3.7	0.04
	Sample 2	1.3	1.9	1.8	0.06
	Sample 3	2.6	2.0	0.9	0.20
4037	Charged + NAP Treated - 3 min				
	Sample 1	5.1	1.1	317.0	0.06
	Sample 2	3.9	3.0	58.0	0.07
	Sample 3	1.6	1.6	14.1	0.03

[1]The initial (I) and final (F) signal ratios, as shown under each column, are calculated from the data in Table 1, Appendix II.

TABLE 6

SECONDARY ION INTENSITY (SIGNAL) RATIOS FOR
DEUTERIUM CHARGED AISI 1062, 4037 AND 4140 STEELS

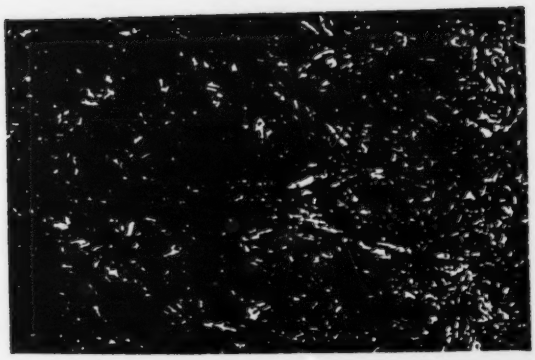
Steel	Condition	Total Sputtered Depth, μm	Signal Ratio[1] $^{1}H/^{56}Fe$ I	$^{1}H/^{56}Fe$ F	$^{2}D/^{56}Fe$ I	$^{2}D/^{56}Fe$ F	$^{63}Cu/^{56}Fe$ I	$^{63}Cu/^{56}Fe$ F
1062	Charged							
	Sample 1	12	0.8	1.0	0.30	0.8	3.0	0.04
	Sample 2	14	---	---	0.40	0.6	---	--
	Sample 3		0.7	0.1	1.10	0.1	52.2	0.30
1062	Charged + NAP Treated - 1 min							
	Sample 1	12	1.8	1.6	0.1	0.6	9.3	0.07
	Sample 2	13	1.8	2.4	0.4	0.8	8.3	<0.01
	Sample 3	20	---	---	0.1	0.3	---	--
4037	Charged							
	Sample 1	19	0.6	0.3	0.3	1.7	15.2	0.20
	Sample 2	9	---	---	0.4	0.9	--	--
	Sample 3	20	1.2	0.3	0.5	0.2	10.8	0.05
4037	Charged + NAP Treated - 3 min							
	Sample 1	20	1.4	4.5	0.10	1.0	132.3	9.4
	Sample 2	20	0.7	1.3	0.07	0.2	19.8	0.2
	Sample 3	20	1.9	2.1	0.07	0.3	125.8	3.9
4140	Charged							
	Sample 1	7	0.7	0.04	0.1	0.04	0.06	0.58
	Sample 2	17	0.4	0.07	0.4	0.10	0.23	0.04
	Sample 3	14	0.2	0.13	0.2	0.10	0.53	0.19
4140	Charged + NAP Treated - 3 min							
	Sample 1	8	0.5	4.9	0.07	0.7	5.0	0.20
	Sample 2	17	1.4	1.6	0.18	0.1	5.9	0.10
	Sample 3	20	0.6	1.4	0.02	0.1	5.9	0.11

[1]The initial (I) and final (F) signal ratios, as shown under each column, are calculated from the data in Table 1, Appendix III.

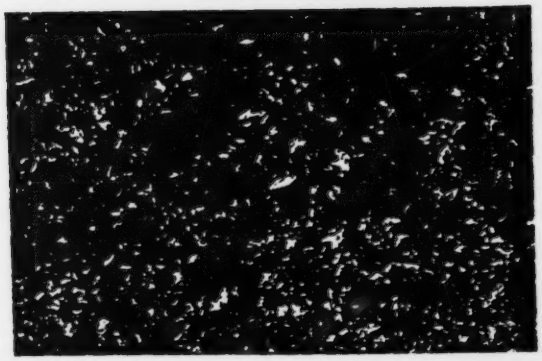
TABLE 7

EFFECT OF NAP TREATMENT ON DEUTERIUM LEVELS IN DEUTERIUM CHARGED STEELS

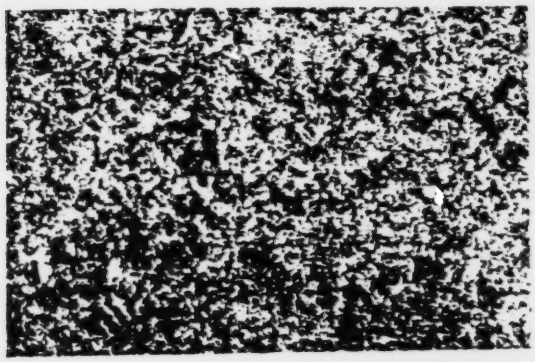
Steel	Deuterium Concentration Atoms/cm^{2}x10^{21} Before NAP Treatment		After NAP Treatment		% Bulk Hydrogen Removed Due to NAP
1062					
Sample 1	6		1.5		
Sample 2	6	avg. 6.0	3.0	avg. 2.8	35
Sample 3	-		4.0		
$\%D_2$ - removed = 53					
4037					
Sample 1	4		0.3		
Sample 2	10	avg. 7.7	1.0	avg. 0.8	65
Sample 3	9		1.0		
$\%D_2$ - removed = 90					
4140					
Sample 1	0.6		0.25		
Sample 2	1.2	avg. 0.7	0.10	avg. 0.4	44
Sample 3	0.3		0.90		
$\%D_2$ - removed = 40					



Neg 8976
1062 Steel



Neg 8977
4037 Steel



Neg 9052
4140 Steel

Figure 1: Photomicrographs of heat treated 1062, 4037 and 4140 steels. Etchant - nital. Magnification 400x.

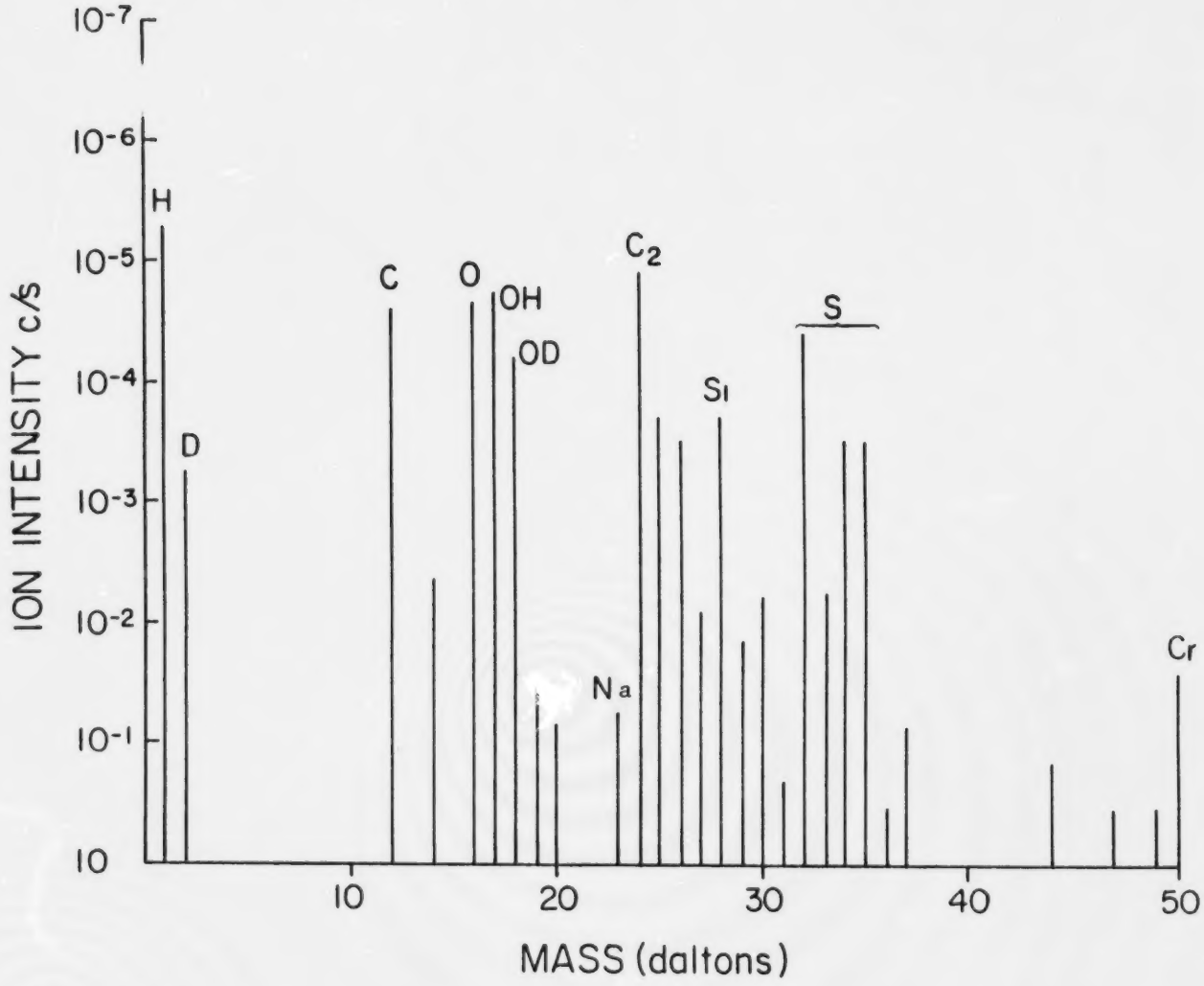


Figure 2: Secondary Ion Mass Spectrum of a 4037 steel surface charged with deuterium. The mass range covered (1-50 daltons) shows hydrogen (protium) from the spectrometer background, deuterium from the surface and a number of minor surface contamimants.

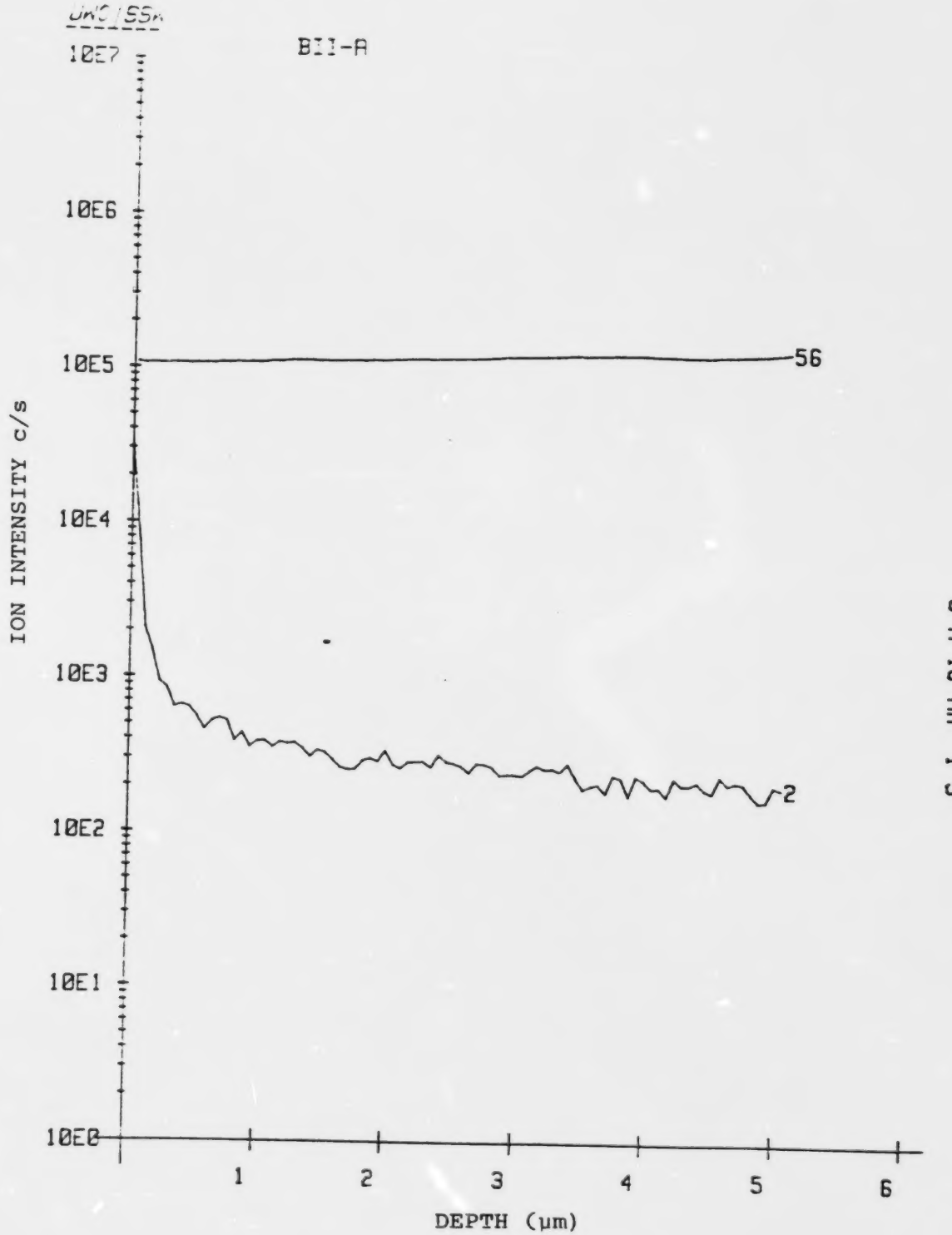


Figure 3: SIMS depth profile of a 4037 steel implanted with a dose of 1×10^{15} at/cm^2 of 30 keV D_2^+.

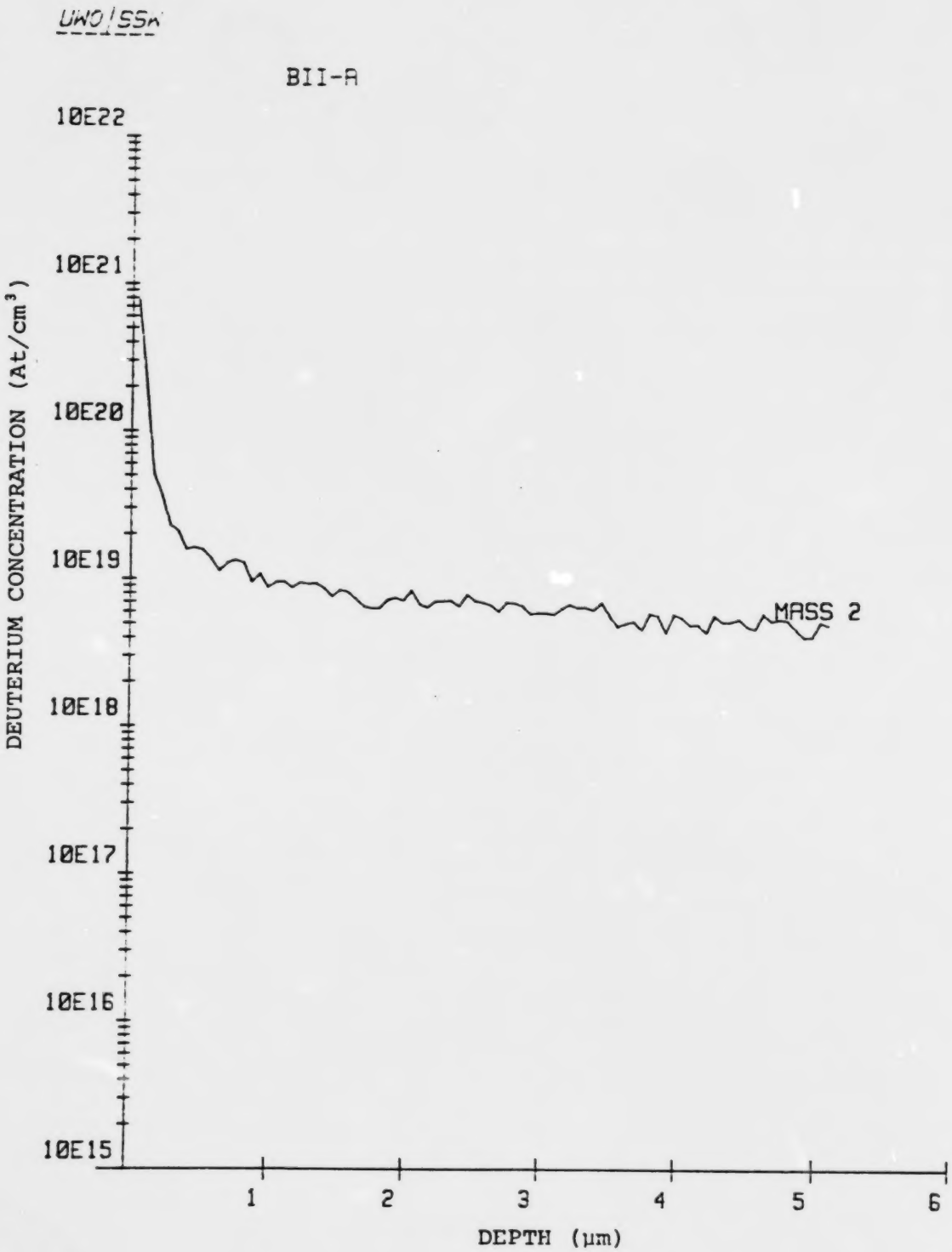


Figure 4: Quantitative plot of deuterium depth profile shown in Figure 2. The calibration constant is 2.5×10^{21}. Concentration of

$$D = 2.5 \times 10^{21} \times \frac{[\ ^{2}D \text{ signal (cps)}\ ]}{[\ ^{56}Fe \text{ signal (cps)}\ ]}$$

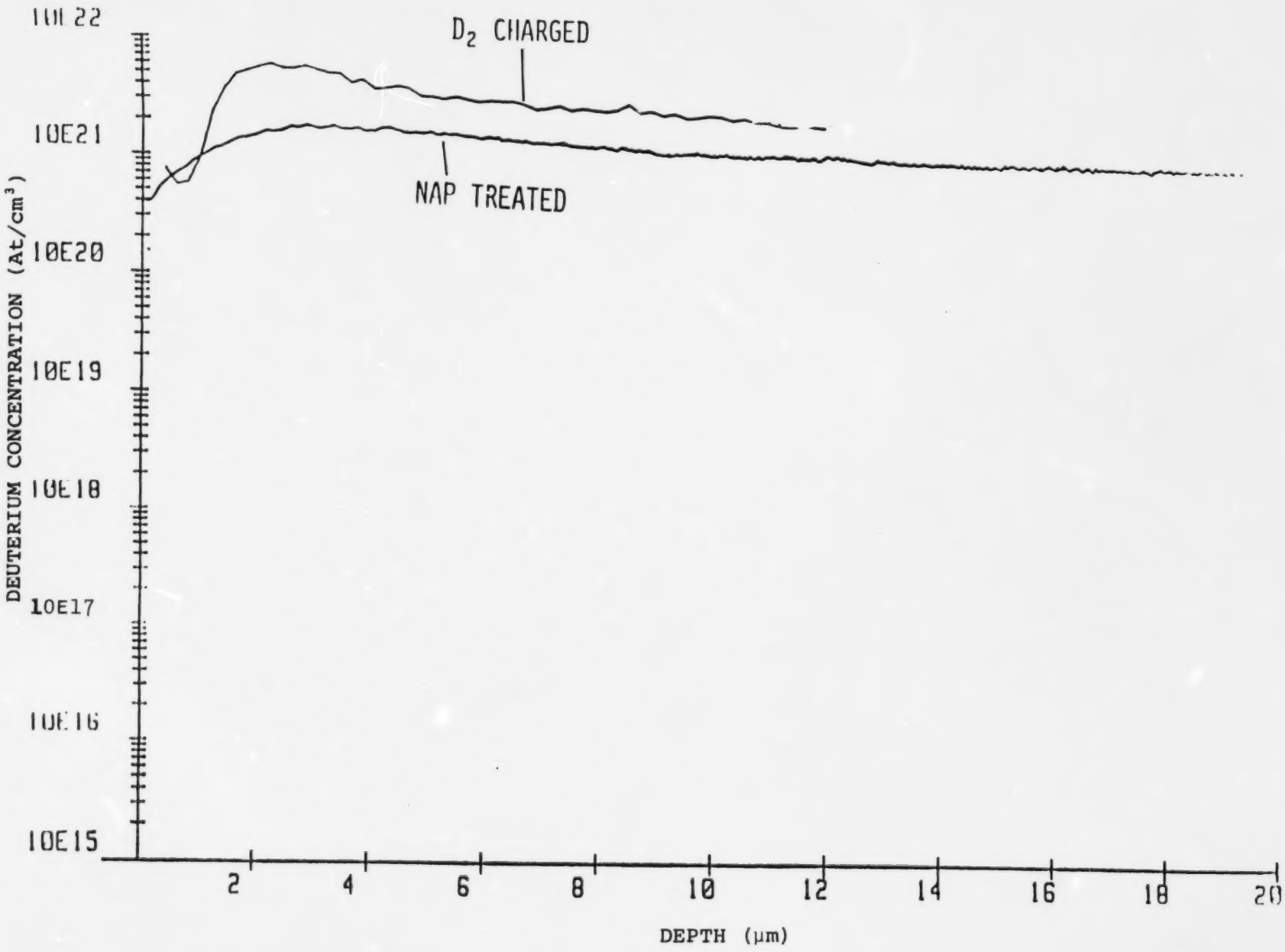


Figure 5: Surface D_2 concentration vs depth (μm) profiles for 1062 steels with and without NAP solution treatment.

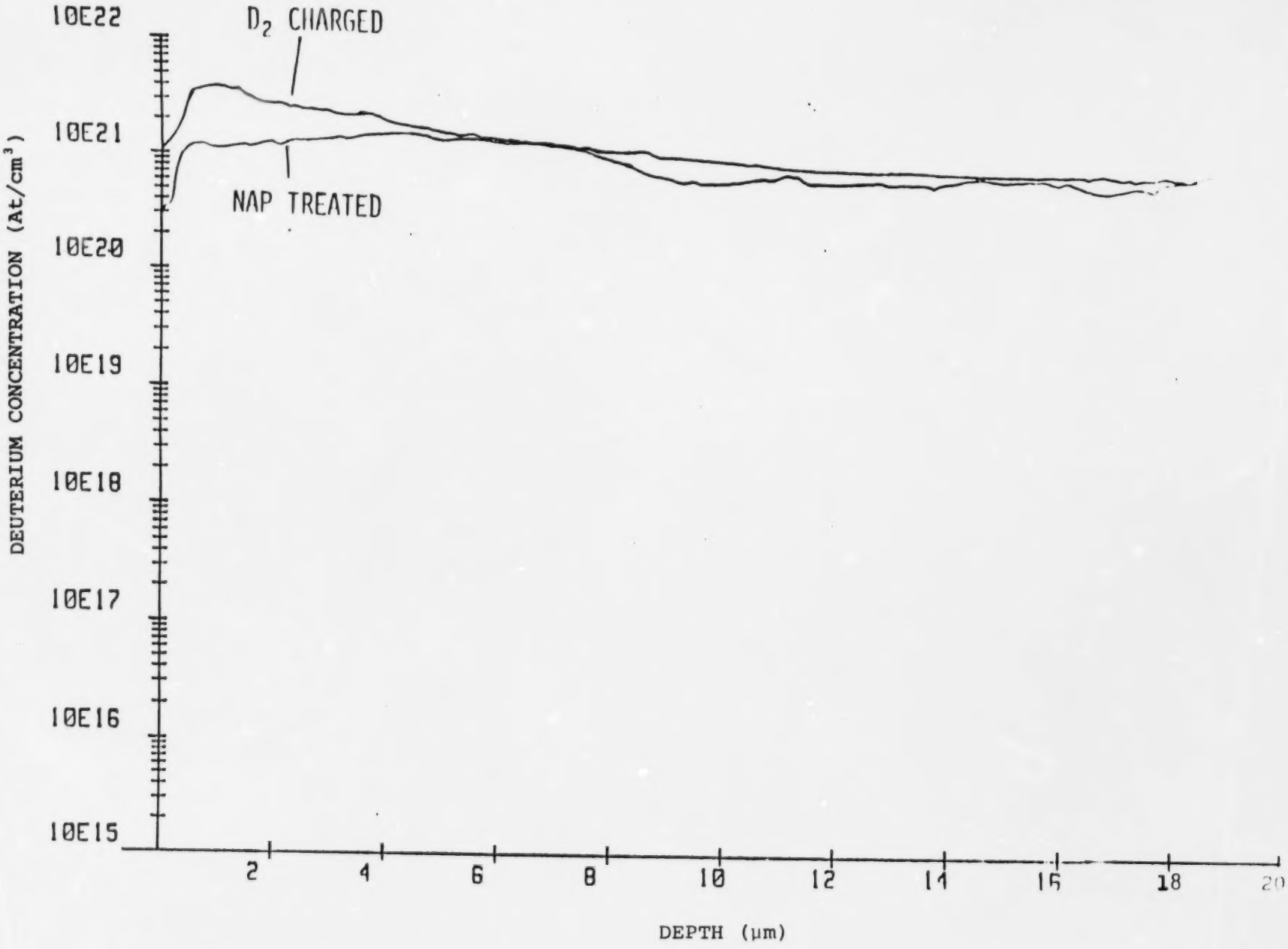


Figure 6: Surface D_2 concentration vs depth (μm) profiles for 4037 steels with and without NAP solution treatment.

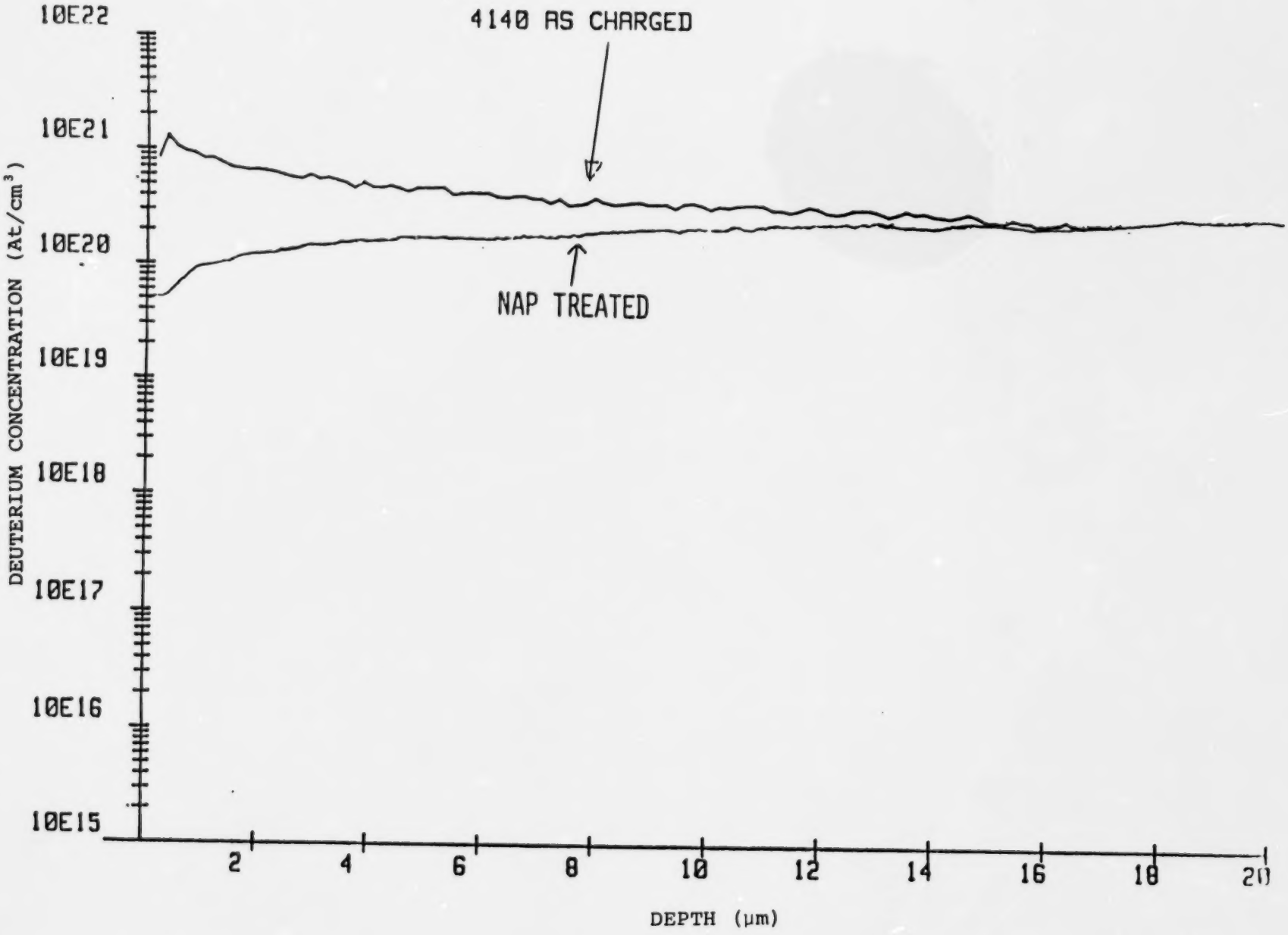


Figure 7: Surface D_2 concentration vs depth (μm) profiles for 4140 steels with and without NAP solution treatment.

APPENDIX I: i) SIMS depth profiles of as-pickled AISI 1062 and 4037 steels. x-axis: Time/s; y-axis: Intensity/Counts per Second

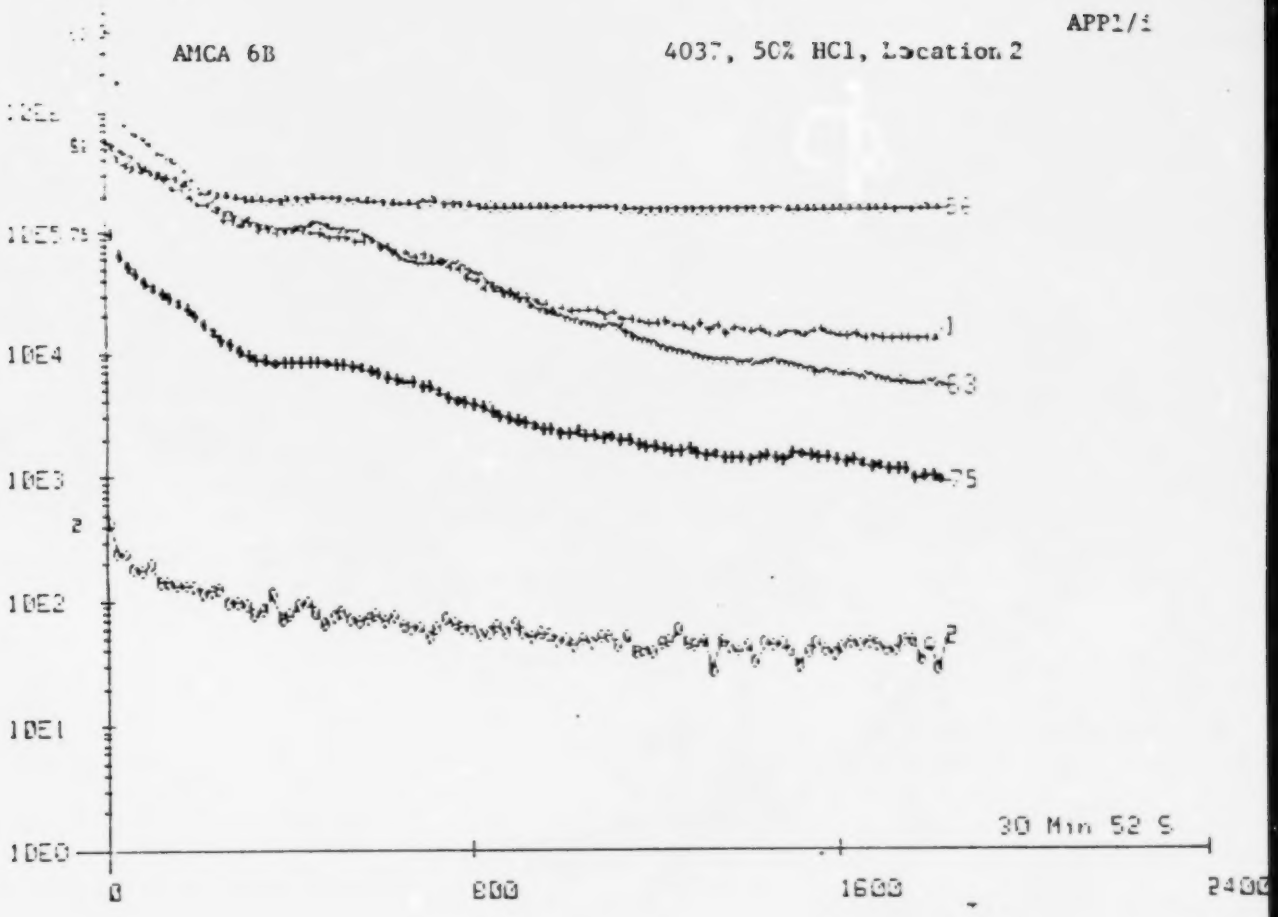
ii) Table 1: Iron, hydrogen, deuterium and copper secondary ion signal intensities in as-pickled AISI 1062 and 4037 steels.

Pickling acids are: i) 50% hydrochloric acid; ii) NA - Nitric + Acetic acid + water; iii) NAP - Nitric + Acetic + Phosphoric acid + water. Pickling time = 1 minute.

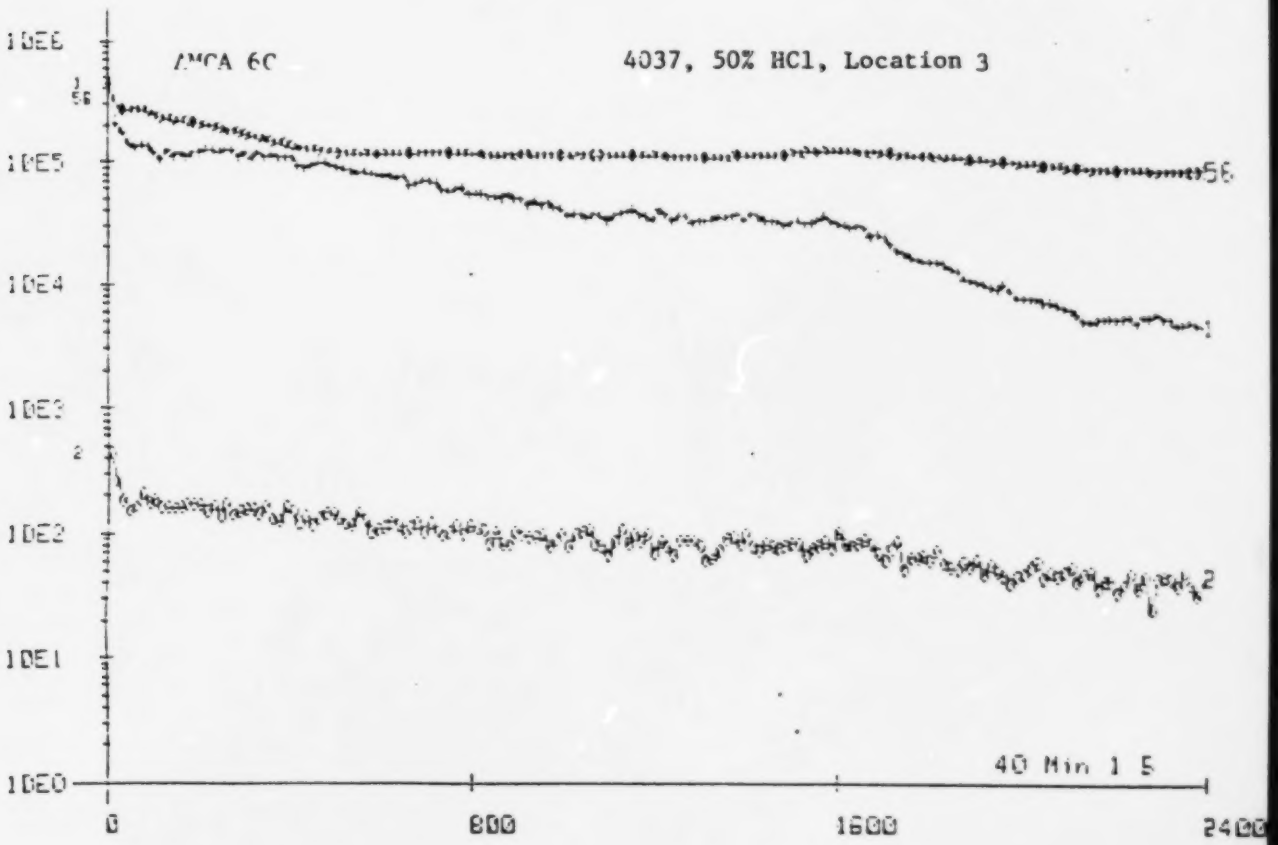
In each figure of this Appendix the individual profiles are designated as follows:

1 = mass 1 - Hydrogen
2 = Deuterium isotope (traces)
56 = Iron
63 = Copper
75 = Silicon oxide ion (SiO_2^-)

AMCA 6B 4037, 50% HCl, Location 2

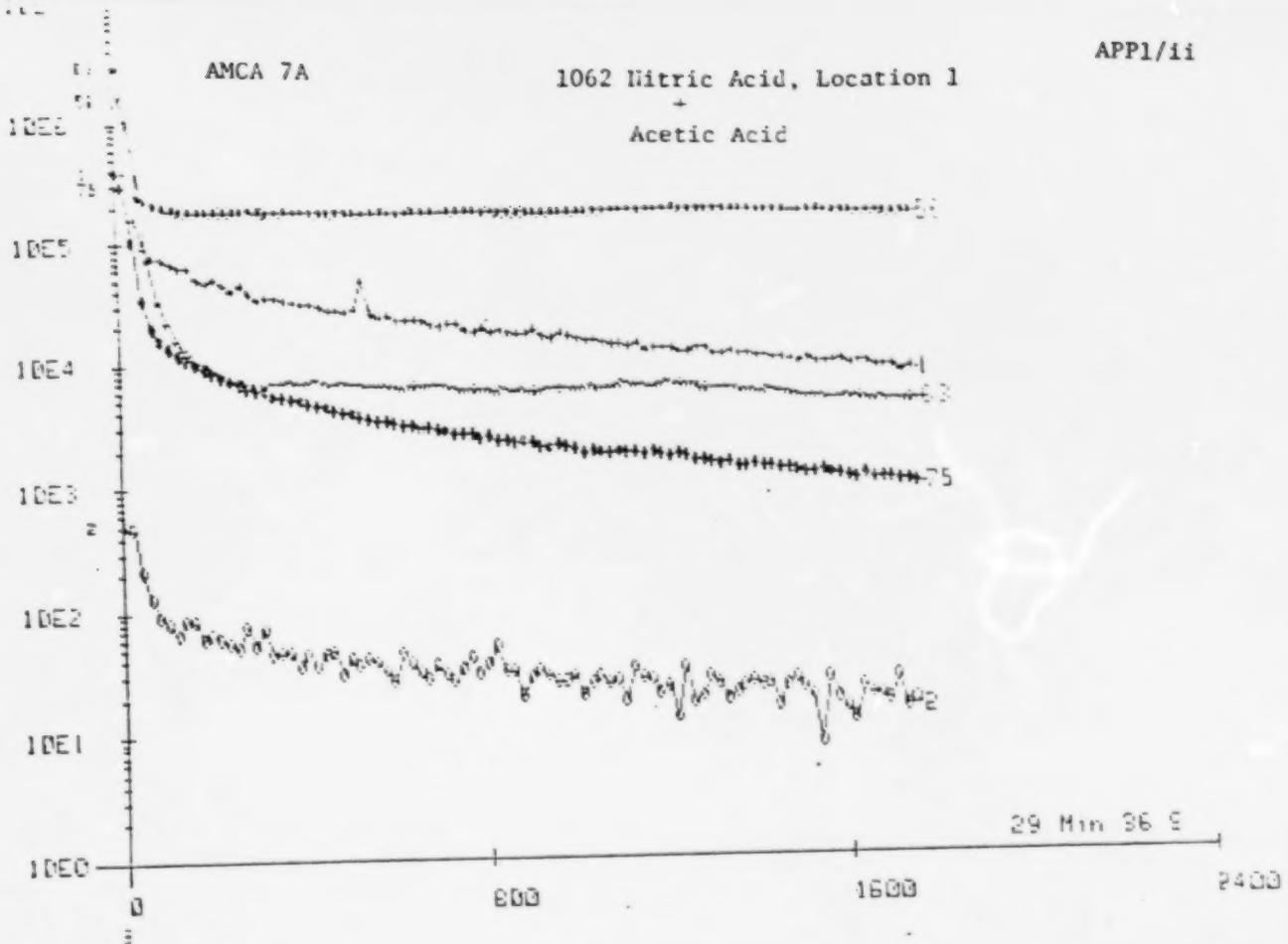


AMCA 6C 4037, 50% HCl, Location 3



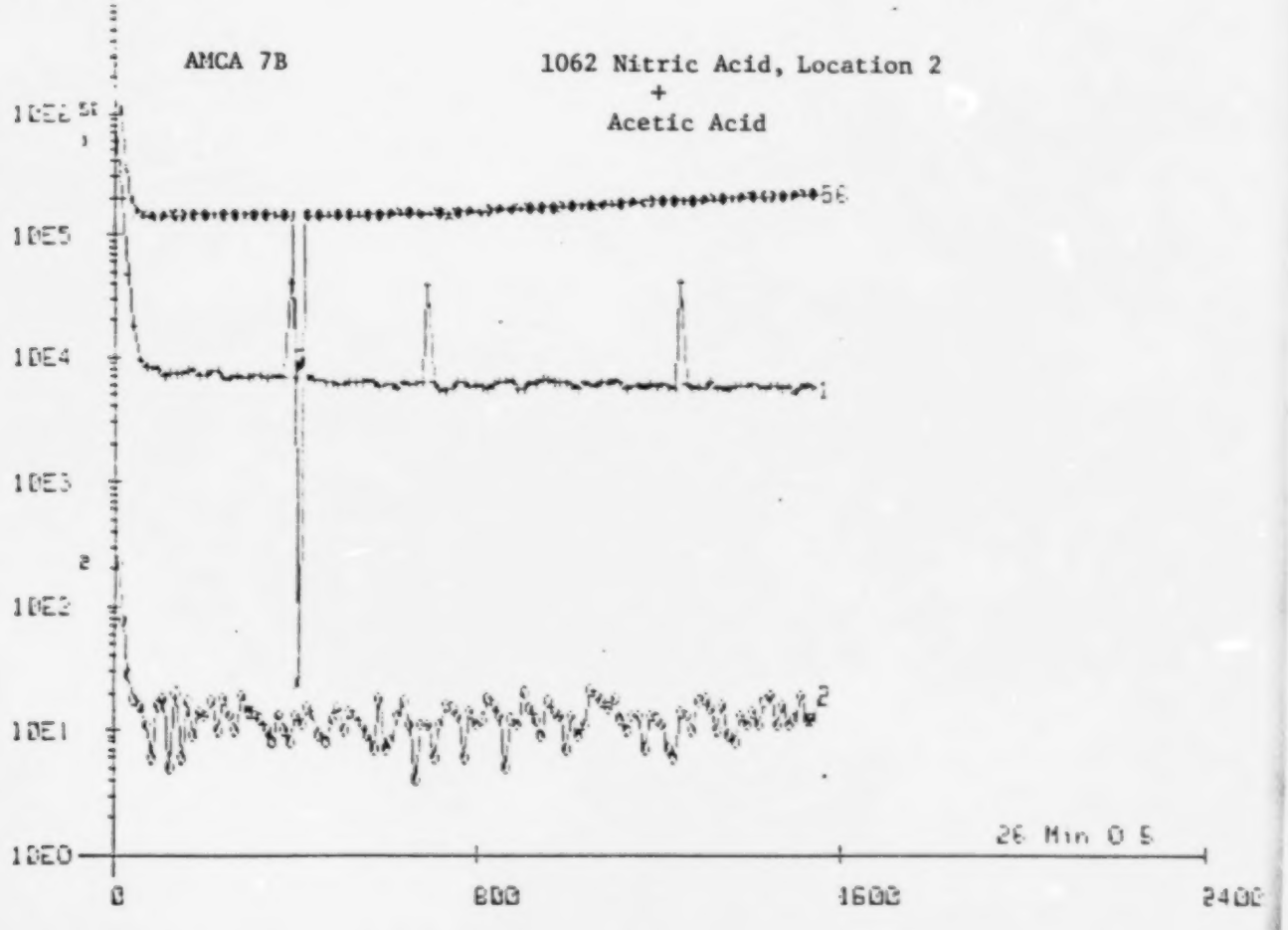
AMCA 7A

1062 Nitric Acid, Location 1
+
Acetic Acid



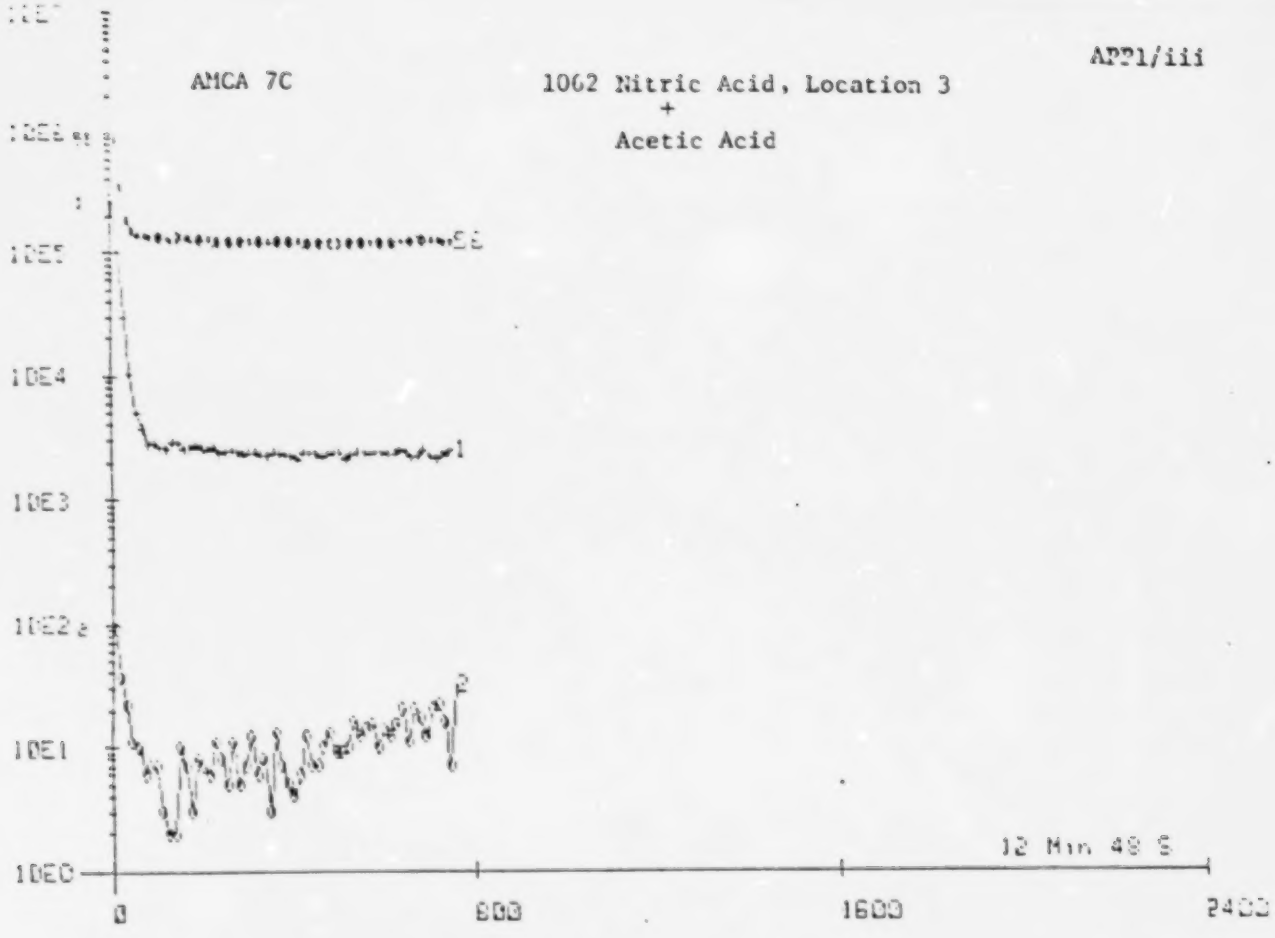
AMCA 7B

1062 Nitric Acid, Location 2
+
Acetic Acid



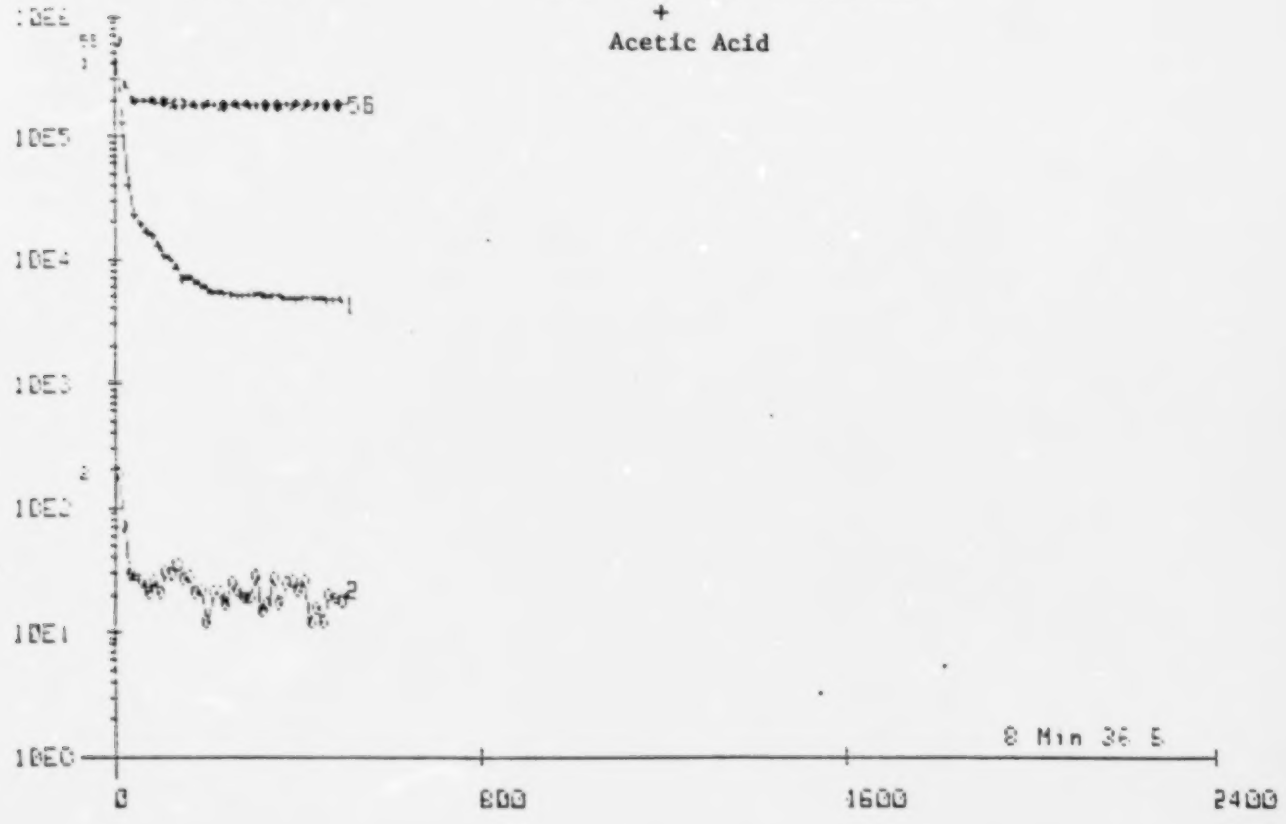
AMCA 7C

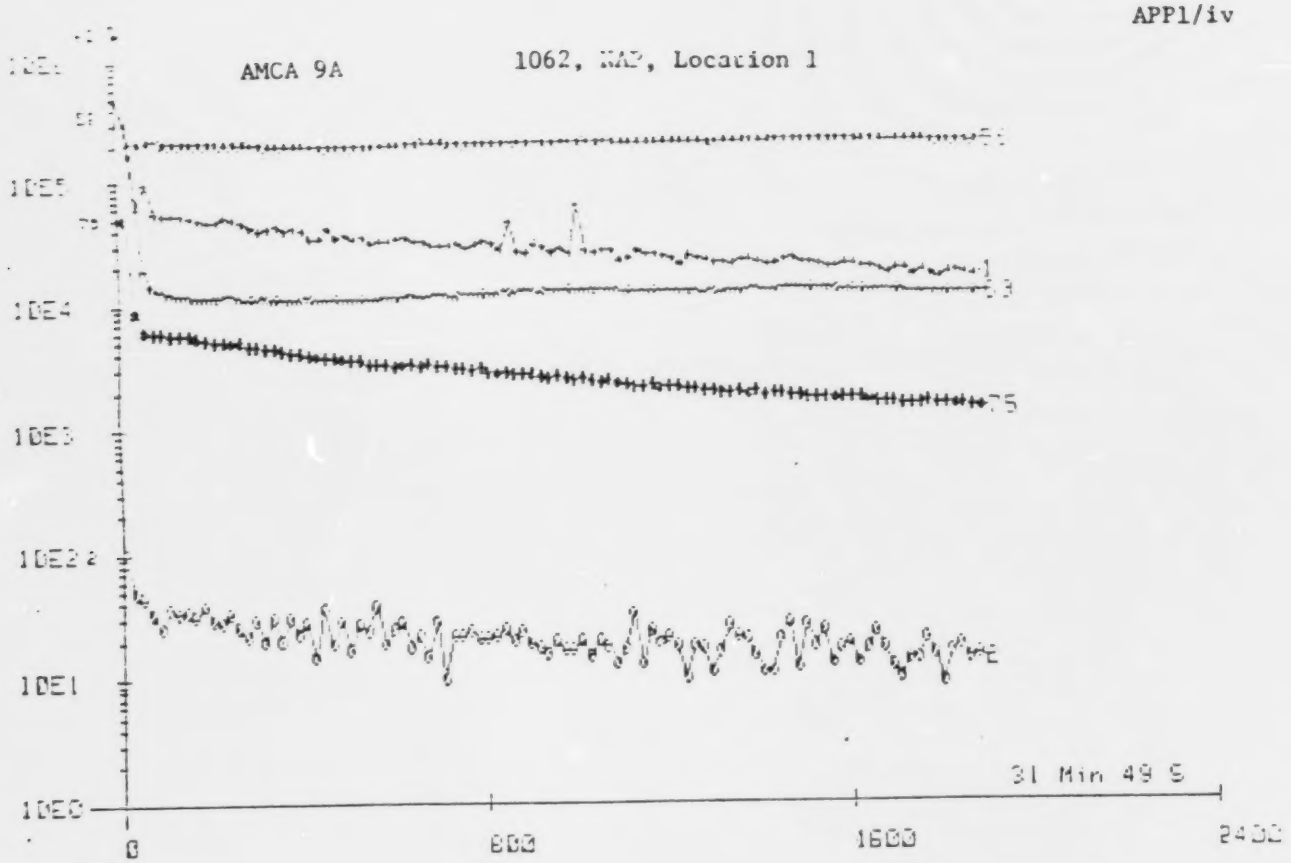
1062 Nitric Acid, Location 3
+
Acetic Acid

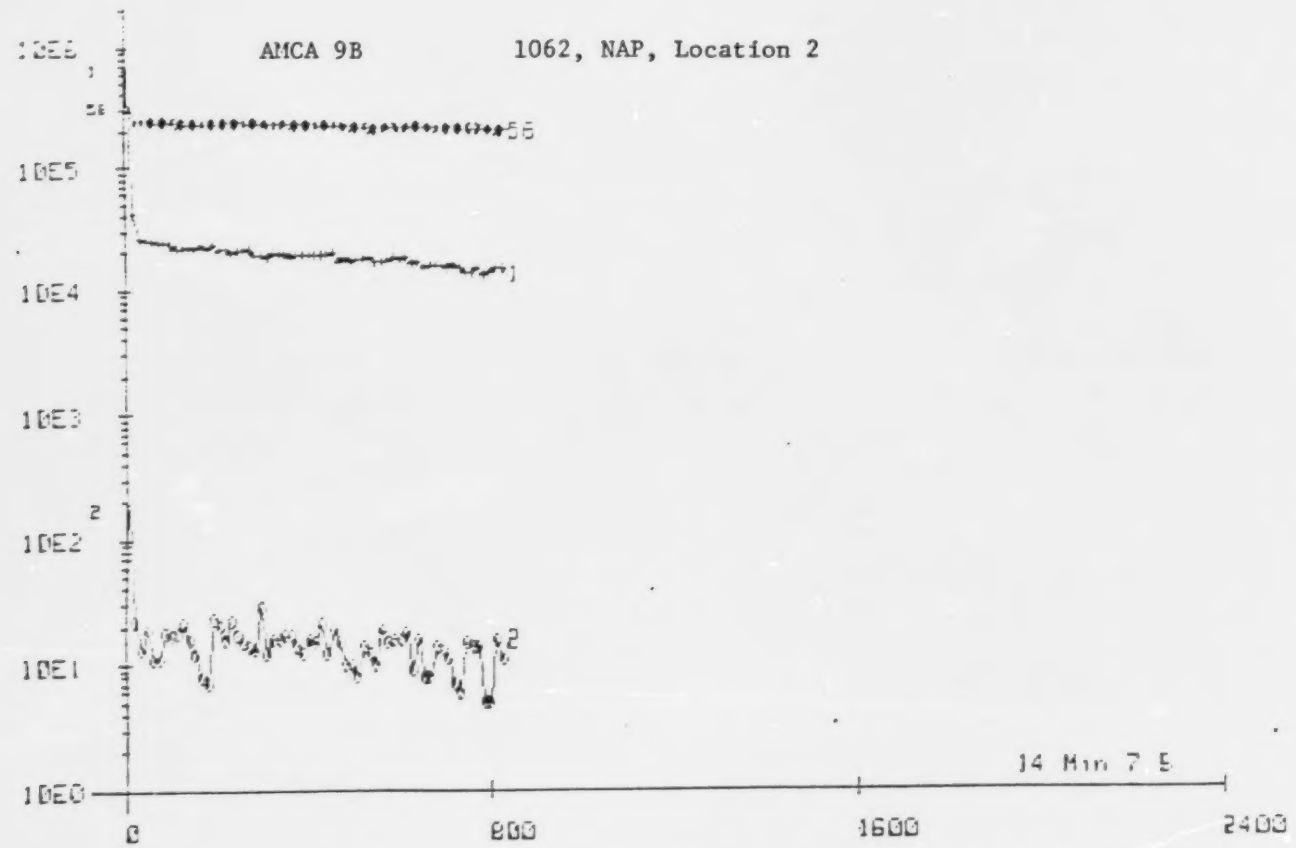


AMCA 7D

1062 Nitric Acid, Location 4
+
Acetic Acid



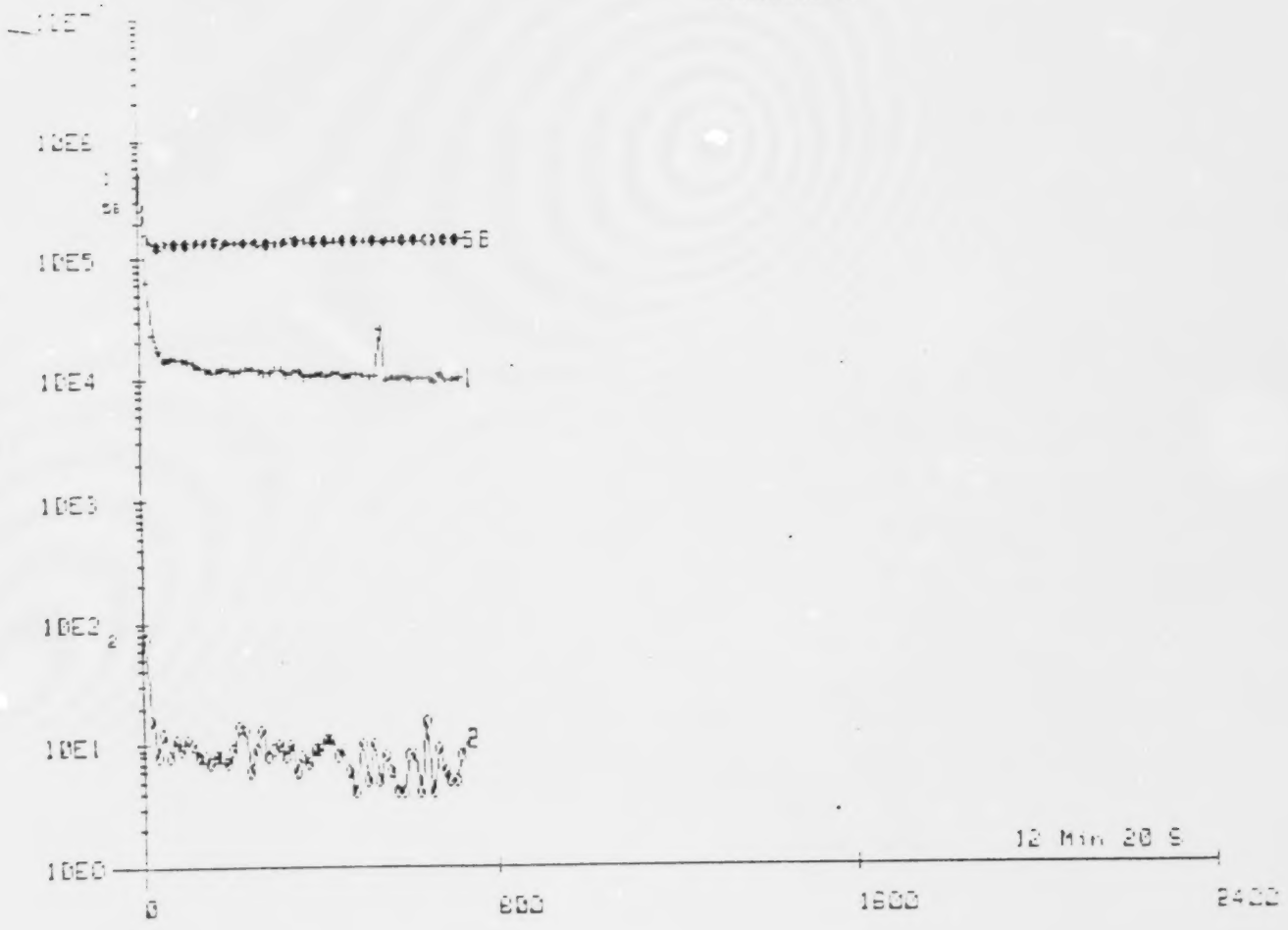

AMCA 9A
1062, NAP, Location 1
10E5
10E4
10E3
10E2
10E1
10E0
31 Min 49 S
0
800
1600
2400

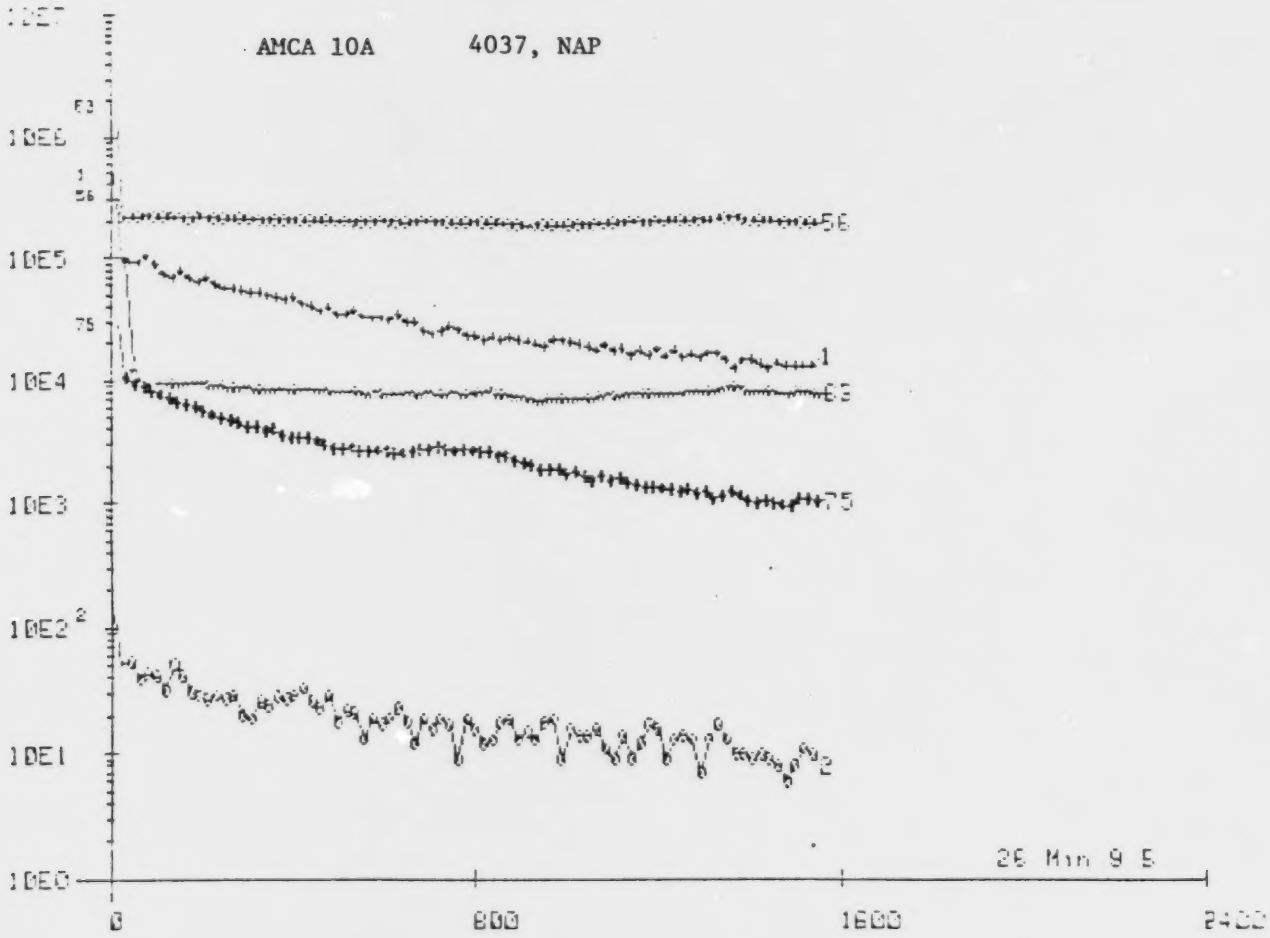

AMCA 9B
1062, NAP, Location 2
10E5
10E4
10E3
10E2
10E1
10E0
14 Min 7 S
0
800
1600
2400

AIICA 8B

4037, Nitric Acid + Acetic Acid

Location 1




AMCA 10A 4037, NAP
10E7
10E6
10E5
10E4
10E3
10E2
10E1
10E0
56
1
75
2
0
800
1600
2400
28 Min 9 S

APPENDIX I: TABLE 1

IRON, HYDROGEN, DEUTERIUM AND COPPER SECONDARY ION SIGNAL INTENSITIES IN DEUTERIUM CHARGED AISI 1062, 4037 AND 4140 STEELS

I = Initial Signal; F = Final Signal

Steel	Condition	Secondary Ion $^{56}Fe^-$ I	$^{56}Fe^-$ F	$^{1}H^-$ I	$^{1}H^-$ F	$^{2}D^-$ I	$^{2}D^-$ F	$^{63}Cu^-$ I	$^{63}Cu^-$ F	Initial Time, s	Final Time, s
4037	50% HCl - 1 min	x10^5		x10^5		x10^2		x10^6			
	Location 1	12.00	2.60	8.50	0.140	7.10	1.50	8.90	0.2800	6	447
	Location 2	5.30	1.50	5.80	0.120	4.30	0.28	4.30	0.0028	6	1848
	Location 3	3.40	0.82	4.50	0.045	4.40	0.45	--	---	5	2400
1062	Nitric + Acetic Acid - 1 min										
	Location 1	16.00	1.50	3.90	0.073	5.10	0.15	3.00	0.0045	6	1775
	Location 2	11.00	2.10	6.00	0.053	2.30	0.11	--	---	6	1560
	Location 3	9.00	1.20	2.60	0.025	0.93	0.07	--	---	6	768
	Location 4	6.40	1.80	4.20	0.042	1.90	0.12	--	---	6	516

.../continued

APPENDIX I: TABLE 1...continued

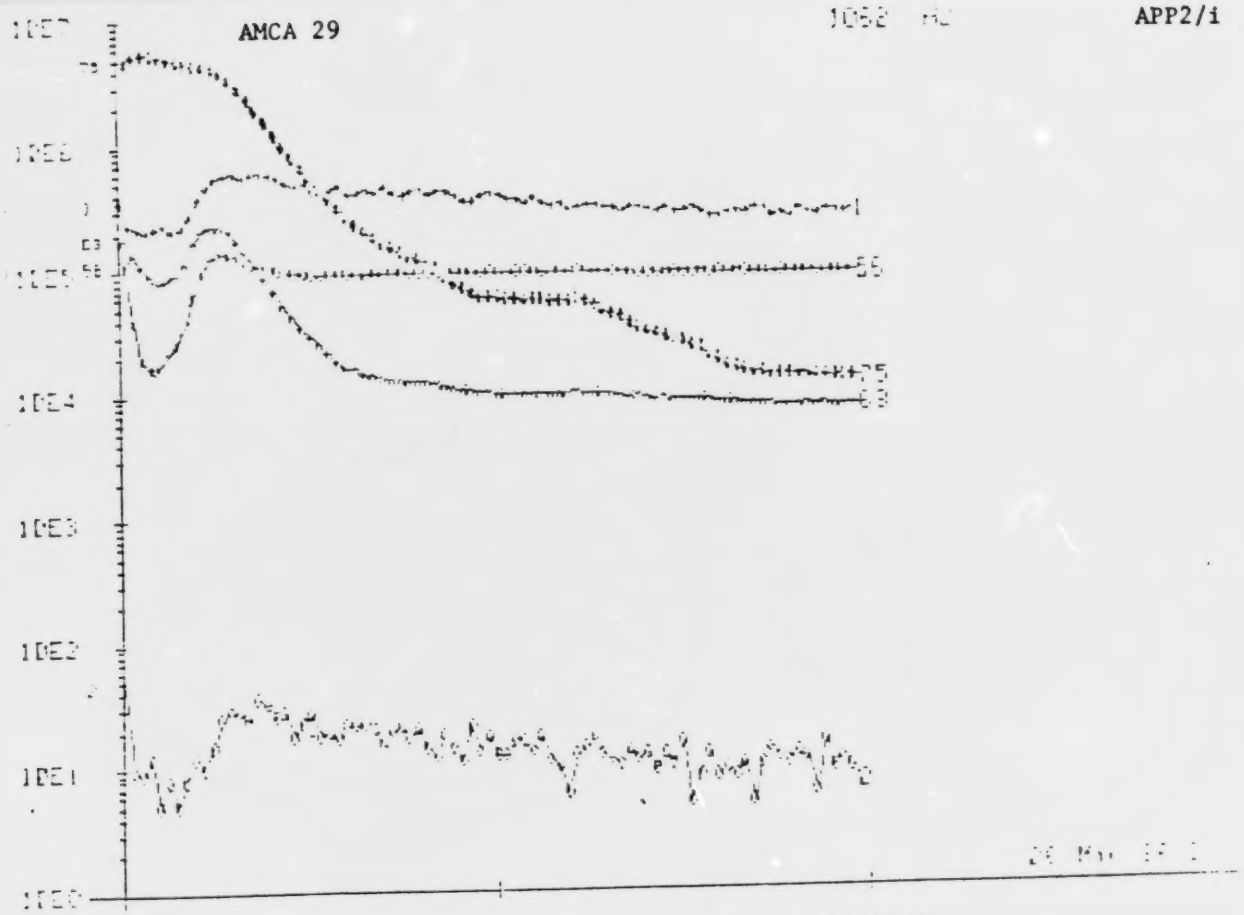
Steel	Condition	Secondary Ion $^{56}Fe^-$ I	$^{56}Fe^-$ F	$^{1}H^-$ I	$^{1}H^-$ F	$^{2}D^-$ I	$^{2}D^-$ F	$^{63}Cu^-$ I	$^{63}Cu^-$ F	Initial Time, s	Final Time, s
4037	Nitric + Acetic Acid	x10^5		x10^5		x10^2		x10^6			
	Location 1	2.80	1.40	5.00	0.099	0.74	0.08	--	---	6	740
	Location 2	4.50	2.20	8.30	0.870	3.60	0.24	--	---		
1062	Nitric + Acetic + Phosphoric Acid - NAP										
	Location 1	3.60	2.00	5.00	0.170	1.00	0.09	1.80	0.012	6	1909
	Location 2	3.20	2.00	6.60	0.130	1.80	0.06	--	---	6	847
4037	Nitric + Acetic + Phosphoric Acid - NAP										
	Location 1	3.30	1.90	5.00	0.130	1.30	0.06	--	---	6	1569

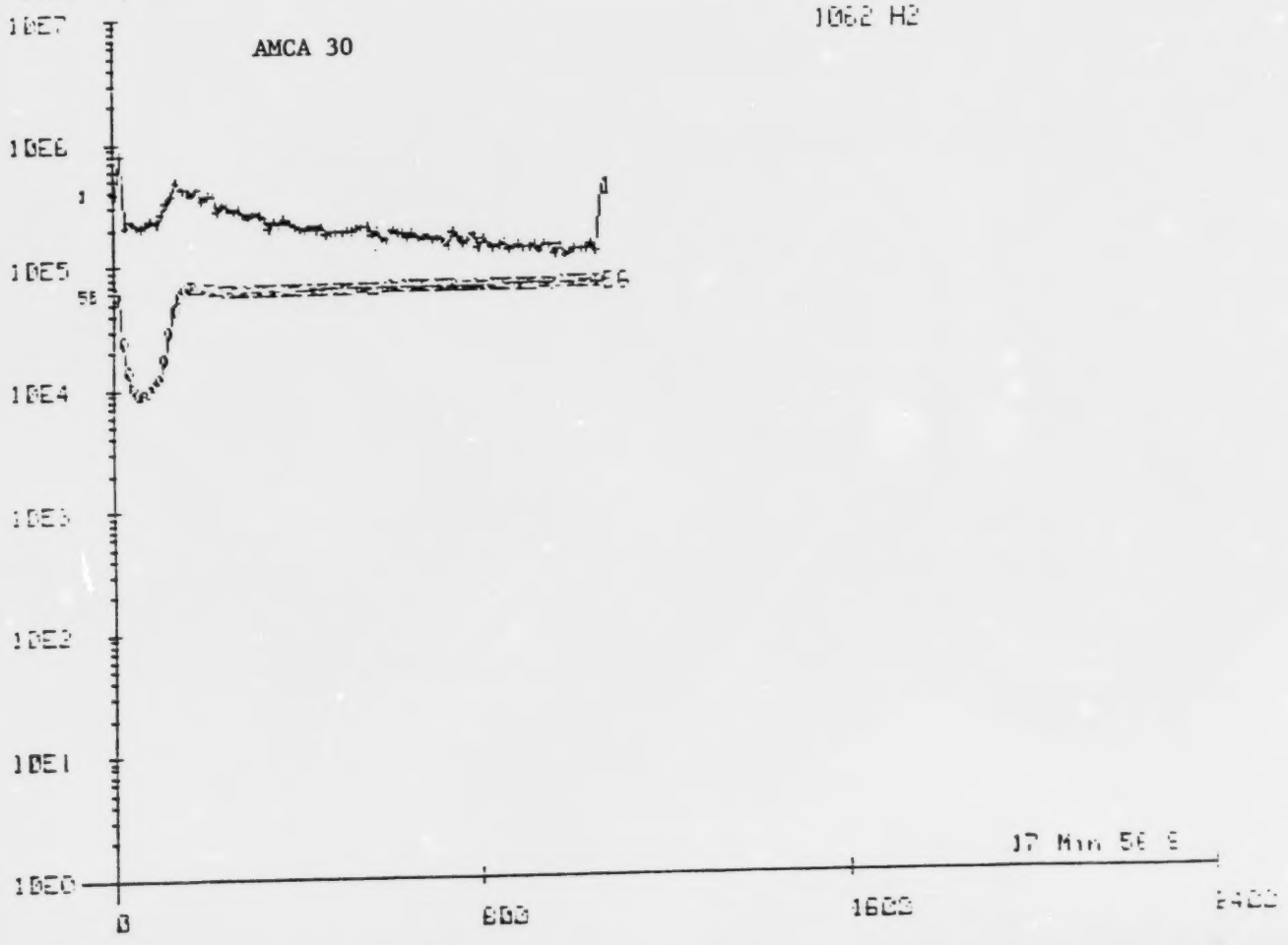
Appendix II: i) SIMS depth profiles of hydrogen charged AISI 1062 and 4037 steels with and without NAP treatment. x-axis: Time/s; y-axis: Intensity/Counts per Second.

ii) Table 1: Iron, hydrogen, deuterium and copper secondary ion signal intensities in hydrogen charged AISI 1062 and 4037 steels.

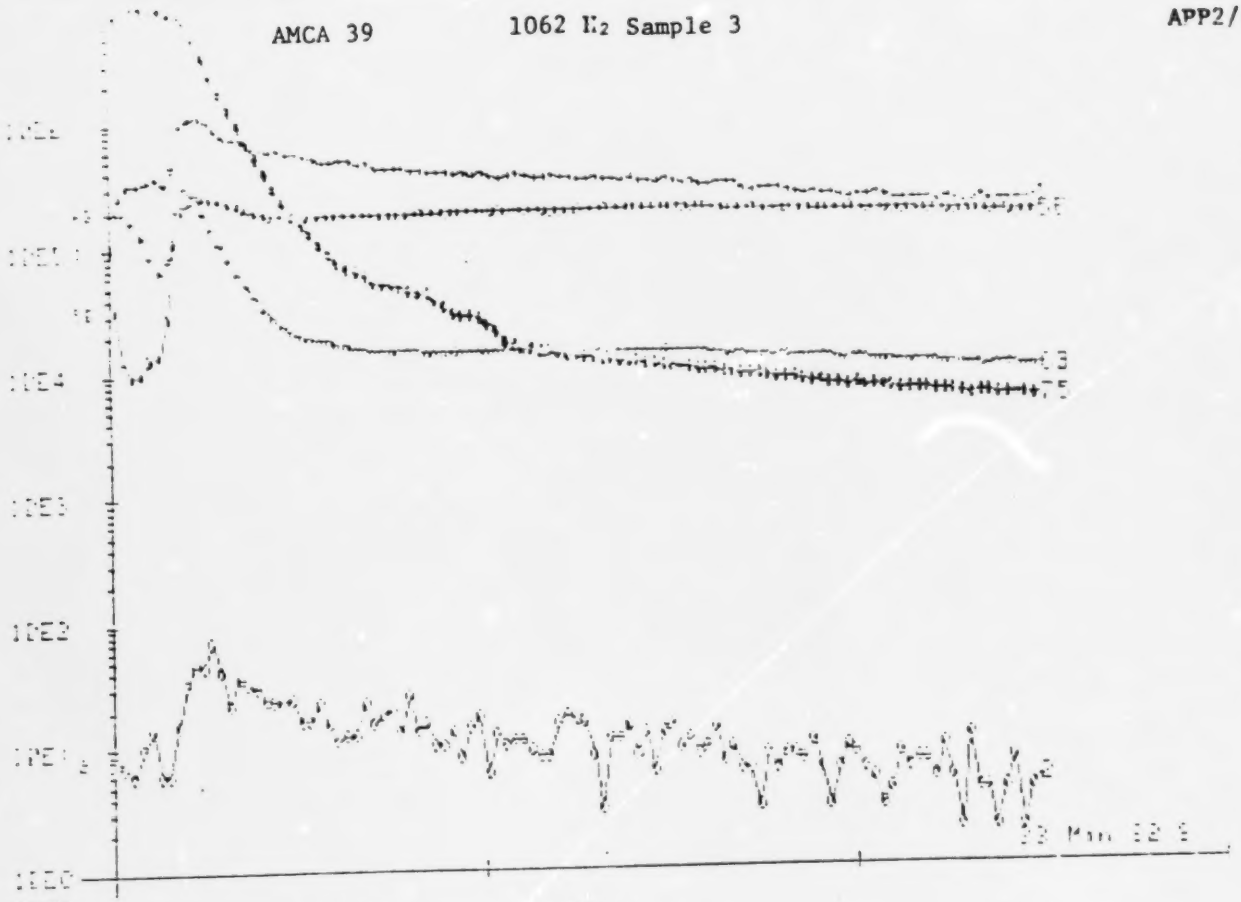
In each figure of Appendix II and III the individual profiles are designated as follows:

1 = mass 1	Hydrogen
2 =	Deuterium
56 =	Iron
63 =	Copper
75 =	Arsenic

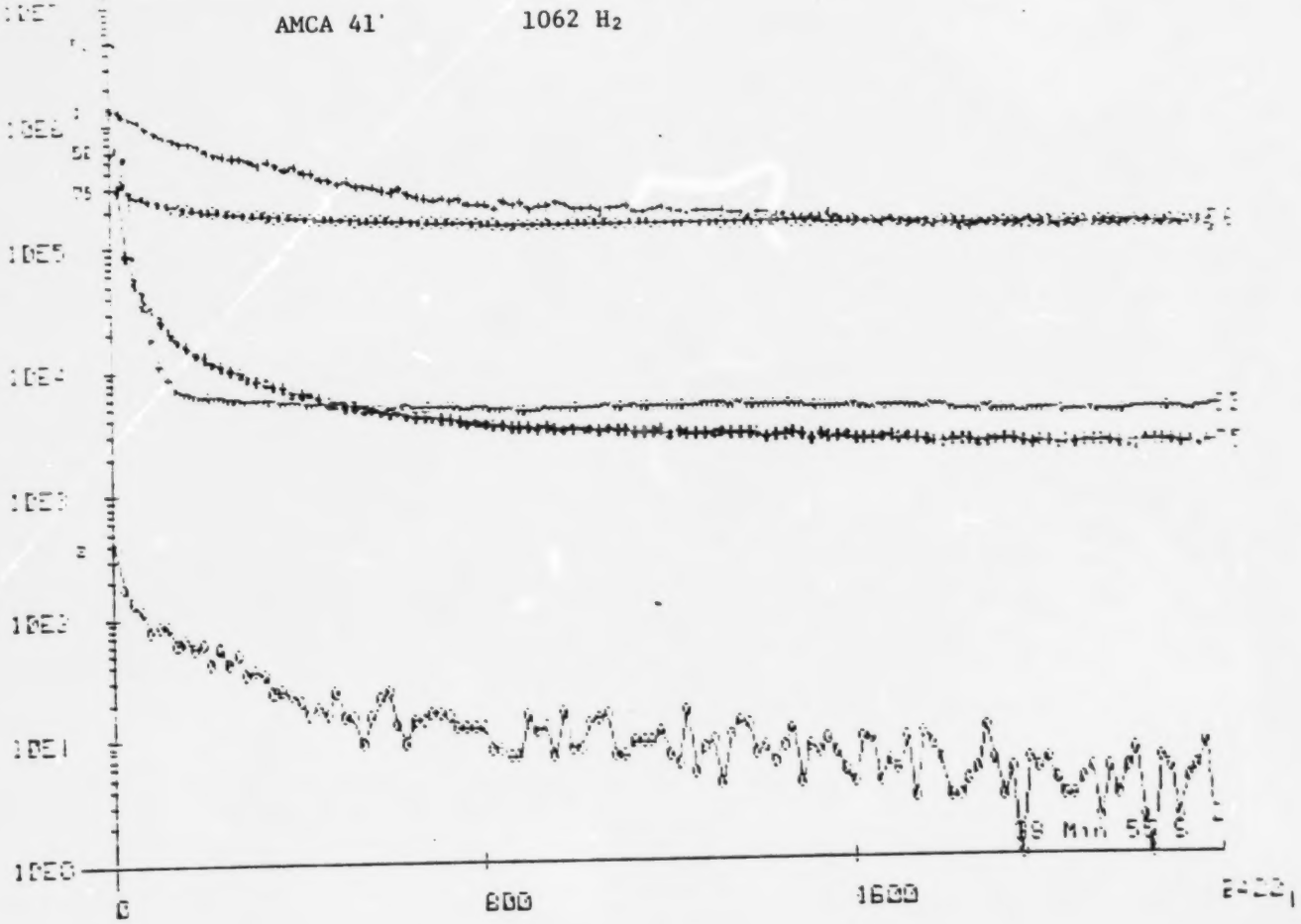

AMCA 29
1062 H2
1E7
1E6
1E5
1E4
1E3
1E2
1E1
1E0

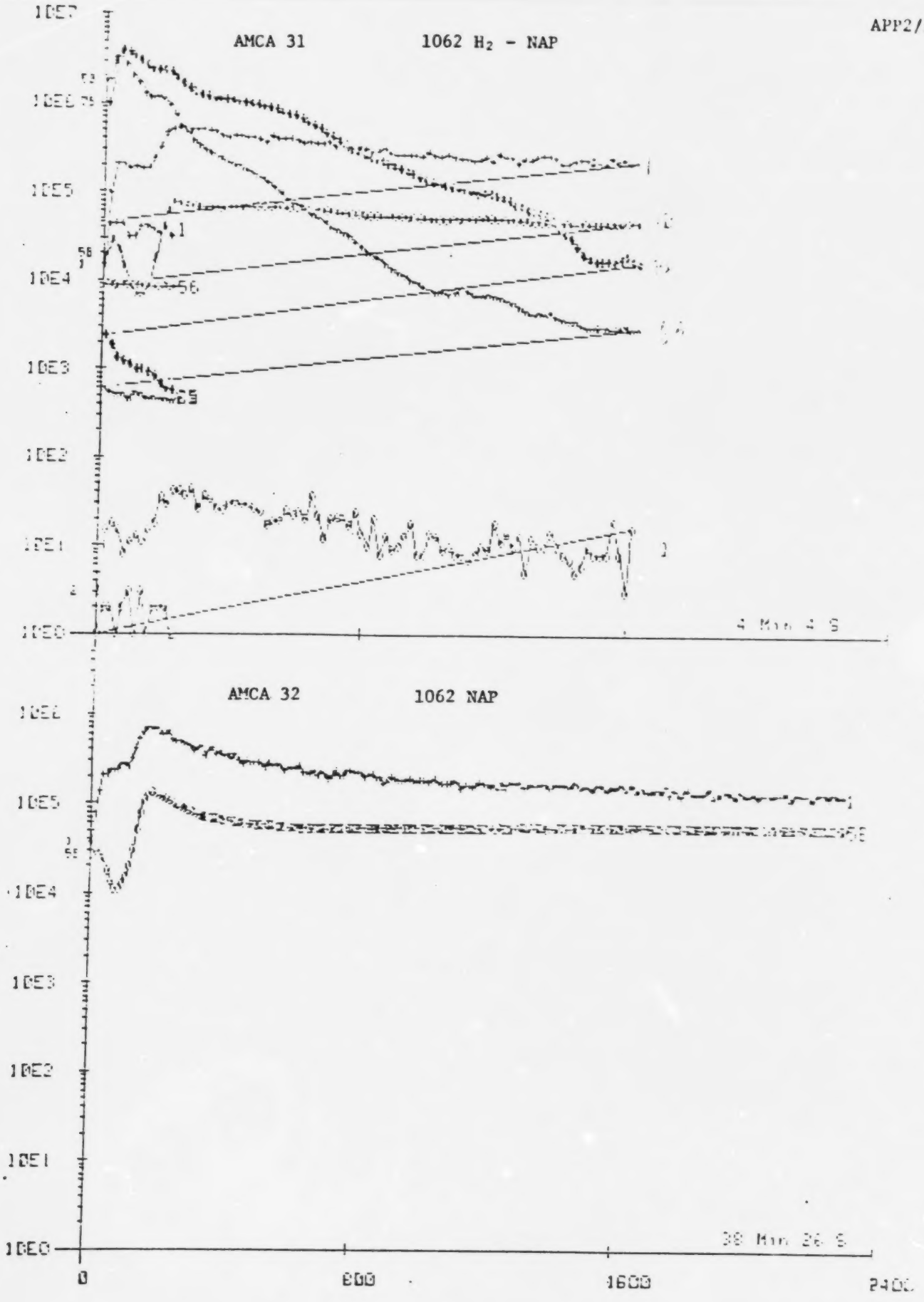

AMCA 30
1062 H2
1E7
1E6
1E5
1E4
1E3
1E2
1E1
1E0
17 Min 56 S
0
800
1600

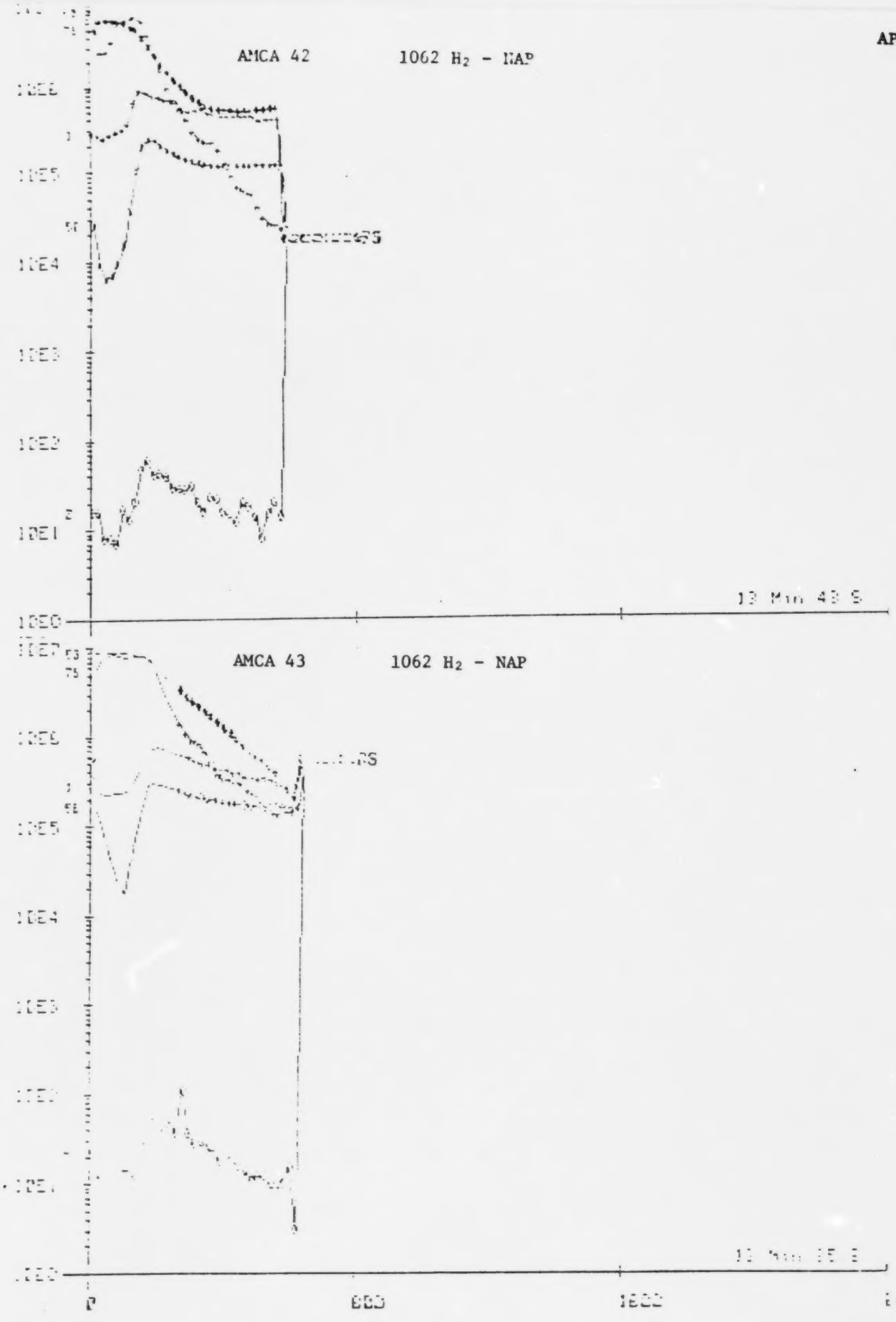
AMCA 39 1062 H_2 Sample 3

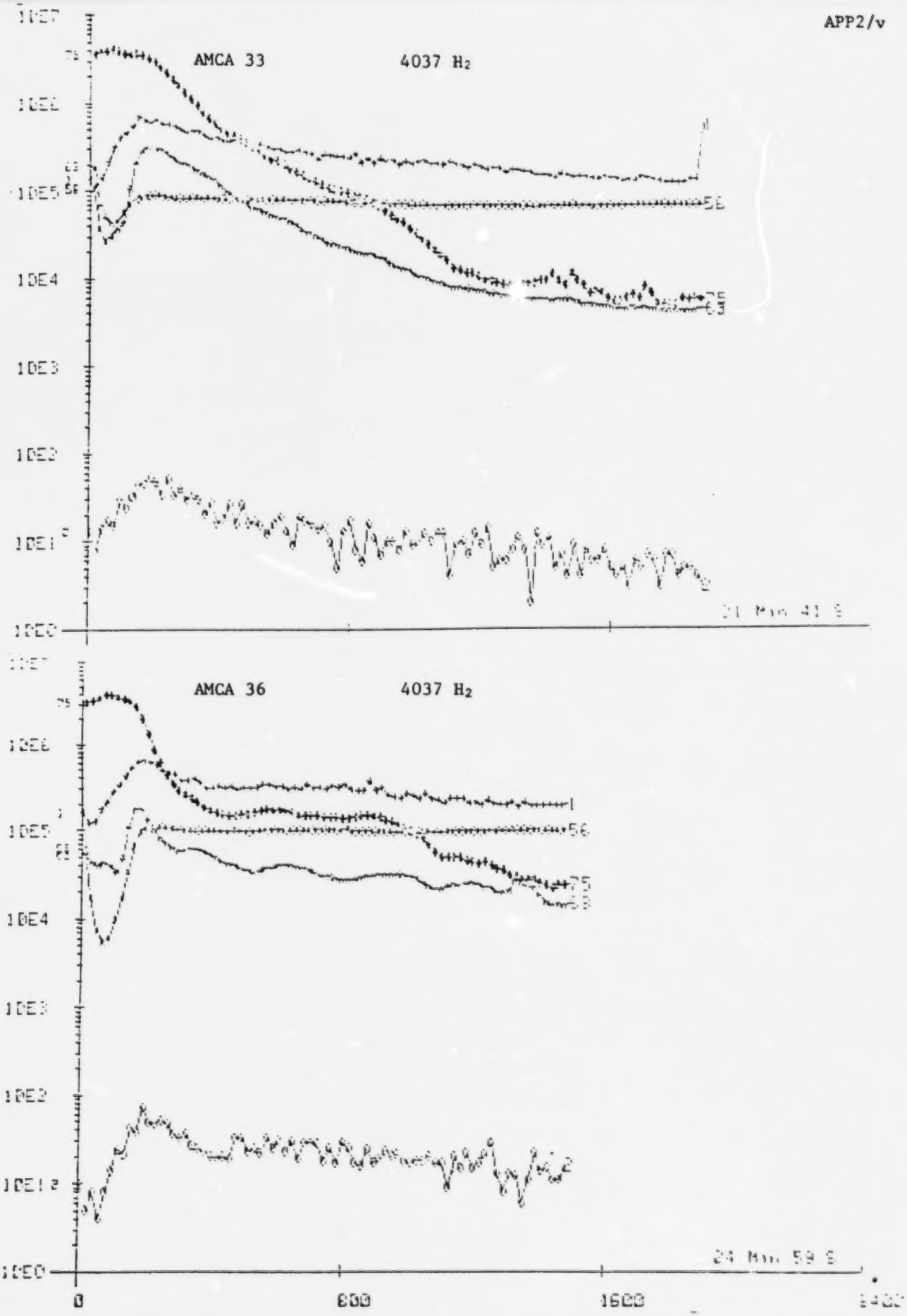


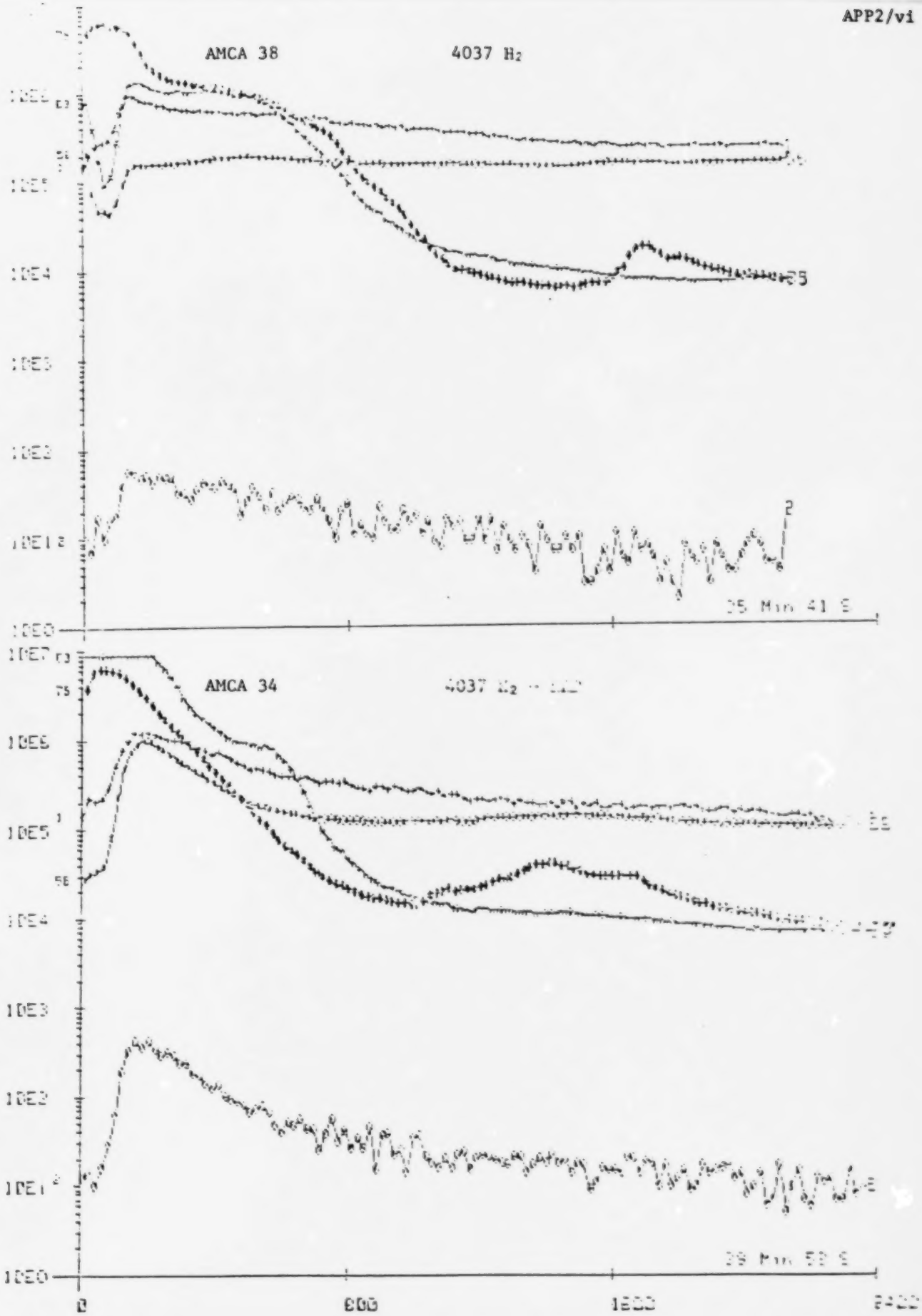
AMCA 41 1062 H_2

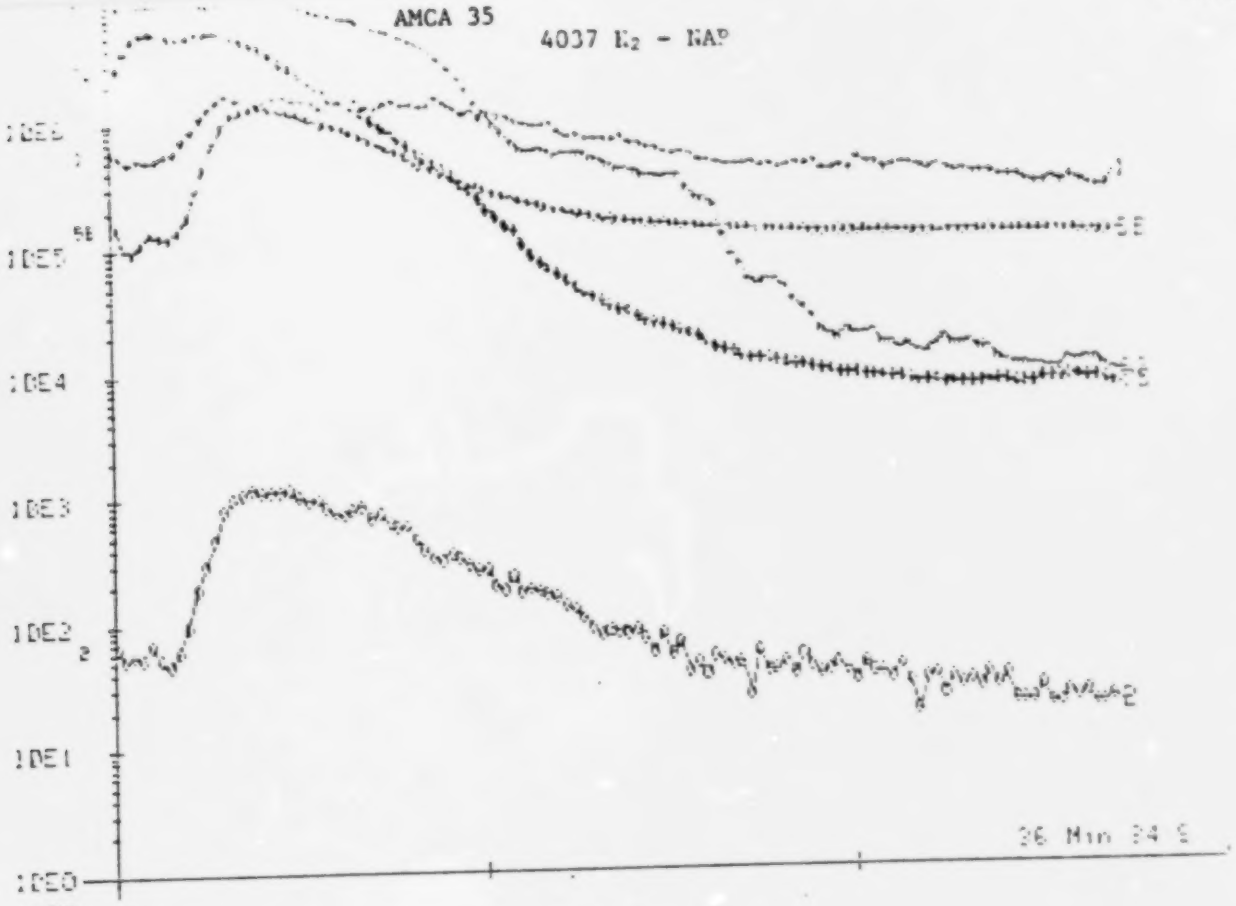


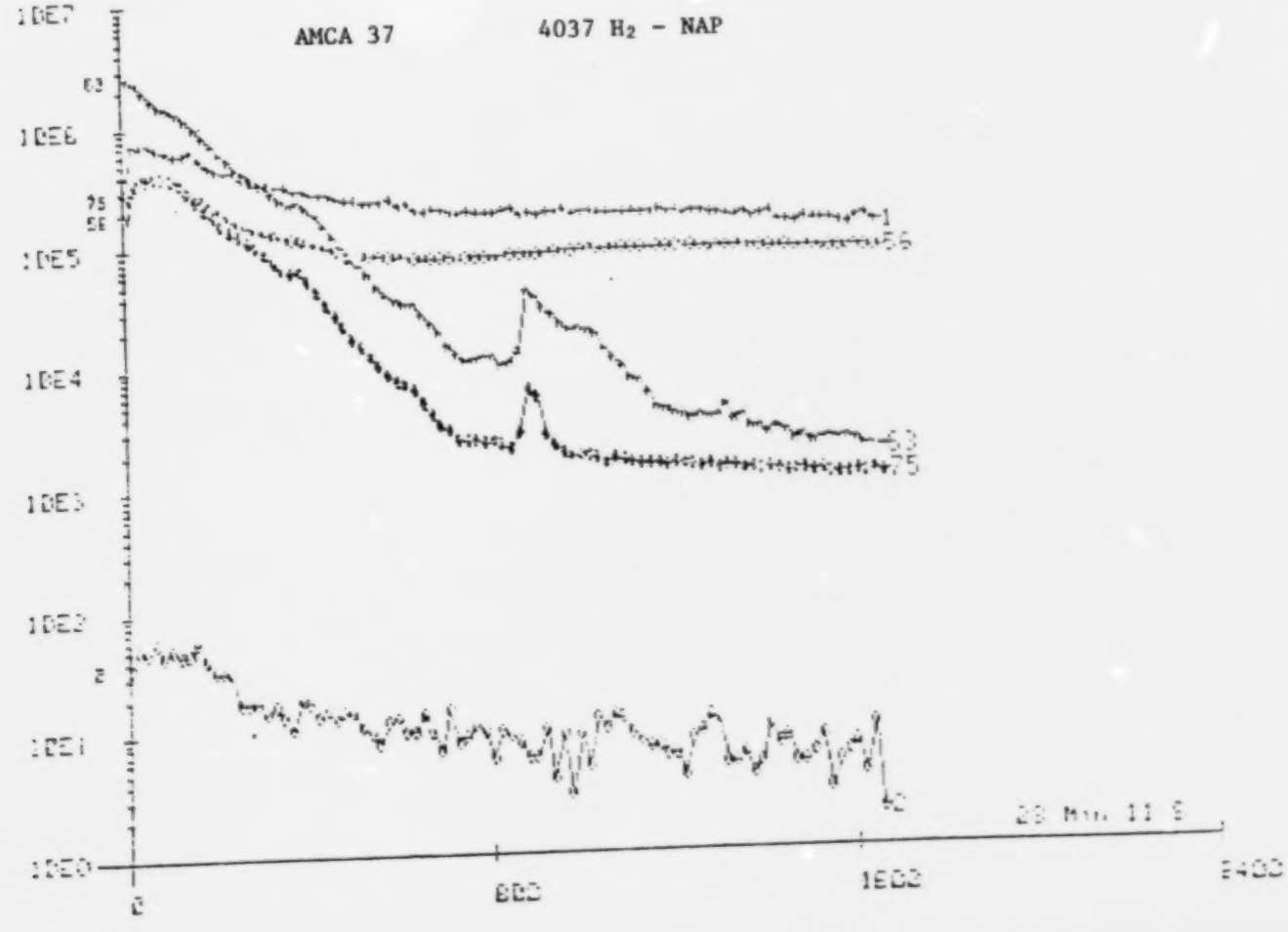

AMCA 31
1062 H_2 - NAP
1E6
1E5
1E4
1E3
1E2
1E1
1E0
4 Min 4 S
AMCA 32
1062 NAP
1E6
1E5
1E4
1E3
1E2
1E1
1E0
38 Min 26 S
0
800
1600
2400


AMCA 42
1062 H_2 - NAP
AMCA 43
1062 H_2 - NAP


AMCA 33
4037 H2
10E7
10E6
10E5
10E4
10E3
10E2
10E1
10E0
21 Min 41 S
AMCA 36
4037 H2
10E7
10E6
10E5
10E4
10E3
10E2
10E1
10E0
24 Min 59 S
0
800
1600


AMCA 38
4037 H2
1DE5
1DE4
1DE3
1DE2
1DE1
1DE0
35 Min 41 S
AMCA 34
1DE7
1DE6
1DE5
1DE4
1DE3
1DE2
1DE1
1DE0
0
800
1600


AMCA 35
4037 H2 - NAP
1DE6
1DE5
1DE4
1DE3
1DE2
1DE1
1DE0
26 Min 34 S


AMCA 37
4037 H2 - NAP
1DE7
1DE6
1DE5
1DE4
1DE3
1DE2
1DE1
1DE0
23 Min 11 S
0
800
1600
2400

APPENDIX II: TABLE 1
IRON, HYDROGEN, DEUTERIUM AND COPPER SECONDARY ION SIGNAL INTENSITIES IN HYDROGEN CHARGED AISI 1062 AND 4037 STEELS

I = Initial Signal; F = Final Signal

		Secondary Ion								Initial	Final
		$^{56}Fe^-$		$^1H^-$		$^2D^-$		$^{63}Cu^-$			
Steel	Condition	I	F	I	F	I	F	I	F	Time, s	Time, s
		x10^5		x10^5		x10^2		x10^5			
1062	Charged										
	Sample 1	1.12	0.86	3.60	2.60	0.47	0.07	1.80	7.40	6	1582
	Sample 2	0.60	0.68	3.93	4.00	--	--	--	--	5	1070
	Sample 3	0.33	1.60	1.01	2.10	0.08	0.02	2.02	0.09	6	2012
	Sample 4	6.28	1.26	13.70	1.18	3.82	0.05	51.24	0.04	6	2400
1062	Charged + NAP Treated - 1 min										
	Sample 1	0.20	0.46	0.15	2.13	0.03	0.16	18.62	0.03	6	1626
	Sample 2	0.27	0.55	3.66	1.25	--	--	--	--	6	2306
	Sample 3	2.55	1.20	2.77	4.07	0.16	--	84.10	0.22	6	582
	Sample 4	1.67	5.59	2.82	5.58	0.25	0.15	89.00	1.43	6	600

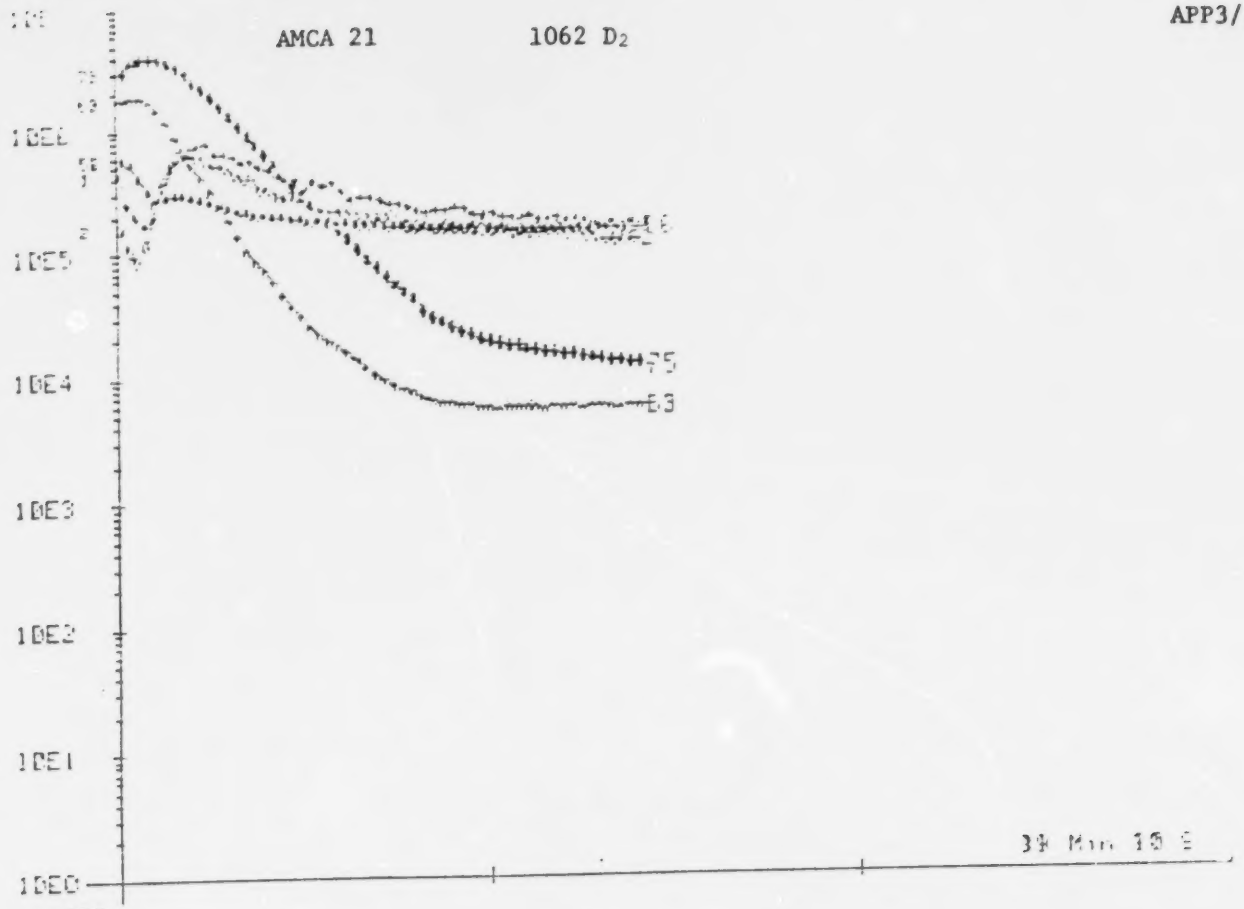
.../continued

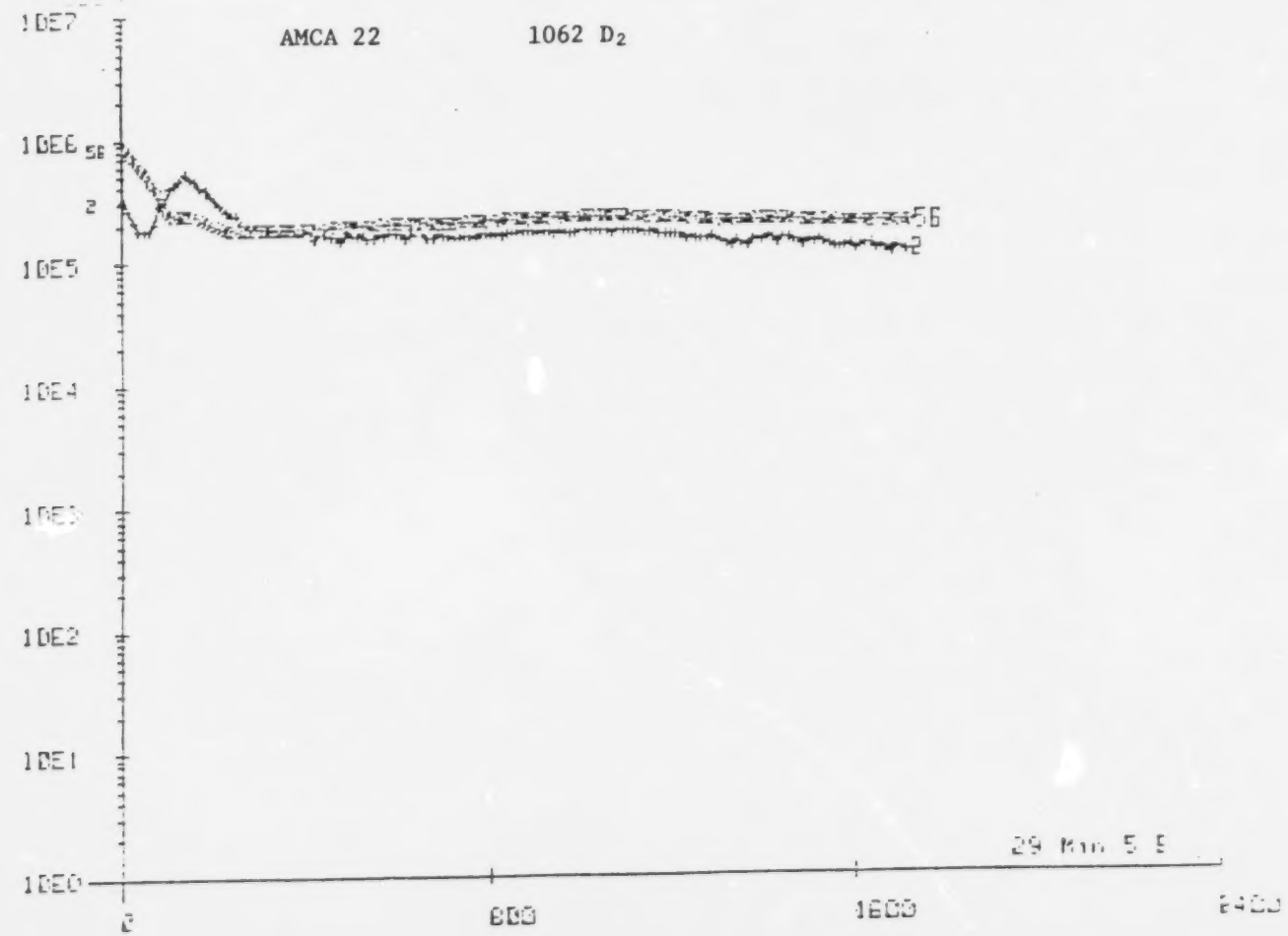
APPENDIX II: TABLE 1...continued

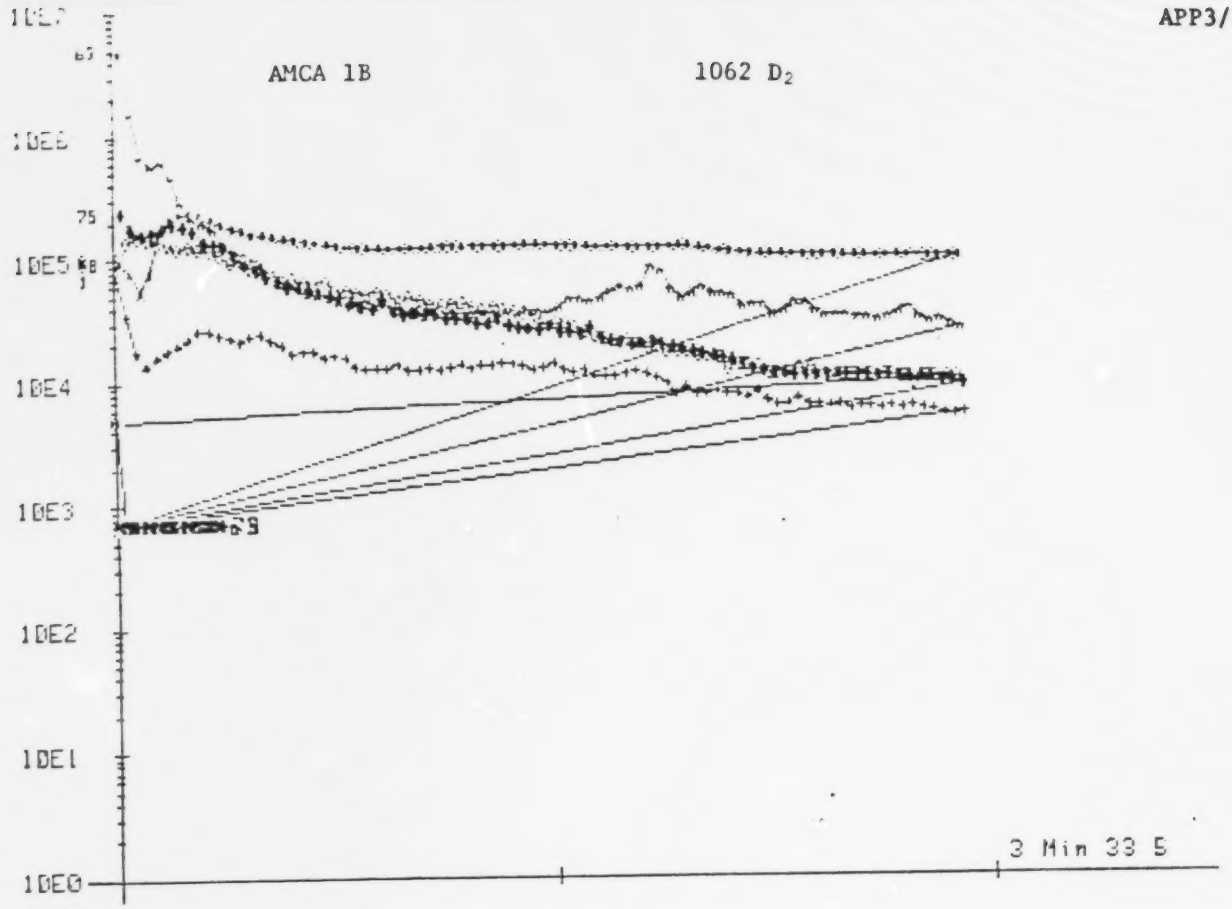
Steel	Condition	Secondary Ion $^{56}Fe^-$ I	$^{56}Fe^-$ F	$^{1}H^-$ I	$^{1}H^-$ F	$^{2}D^-$ I	$^{2}D^-$ F	$^{63}Cu^-$ I	$^{63}Cu^-$ F	Initial Time, s	Final Time, s
4037	Charged	x10^5		x10^5		x10^2		x10^5			
	Sample 1	2.16	1.59	1.54	2.26	0.10	0.19	8.04	0.07	6	2141
	Sample 2	1.07	0.67	1.37	1.29	0.13	0.04	1.93	0.04	6	1900
	Sample 3	0.62	0.98	1.60	1.95	0.10	0.16	0.53	0.15	6	1500
4037	Charged + NAP Treated - 3 min										
	Sample 1	0.28	1.11	1.43	1.22	0.12	0.16	88.69	0.07	6	2393
	Sample 2	1.53	1.10	5.92	3.24	0.67	0.19	88.68	0.08	6	2194
	Sample 3	1.84	0.80	2.95	1.29	0.37	0.02	25.93	0.02	6	1691

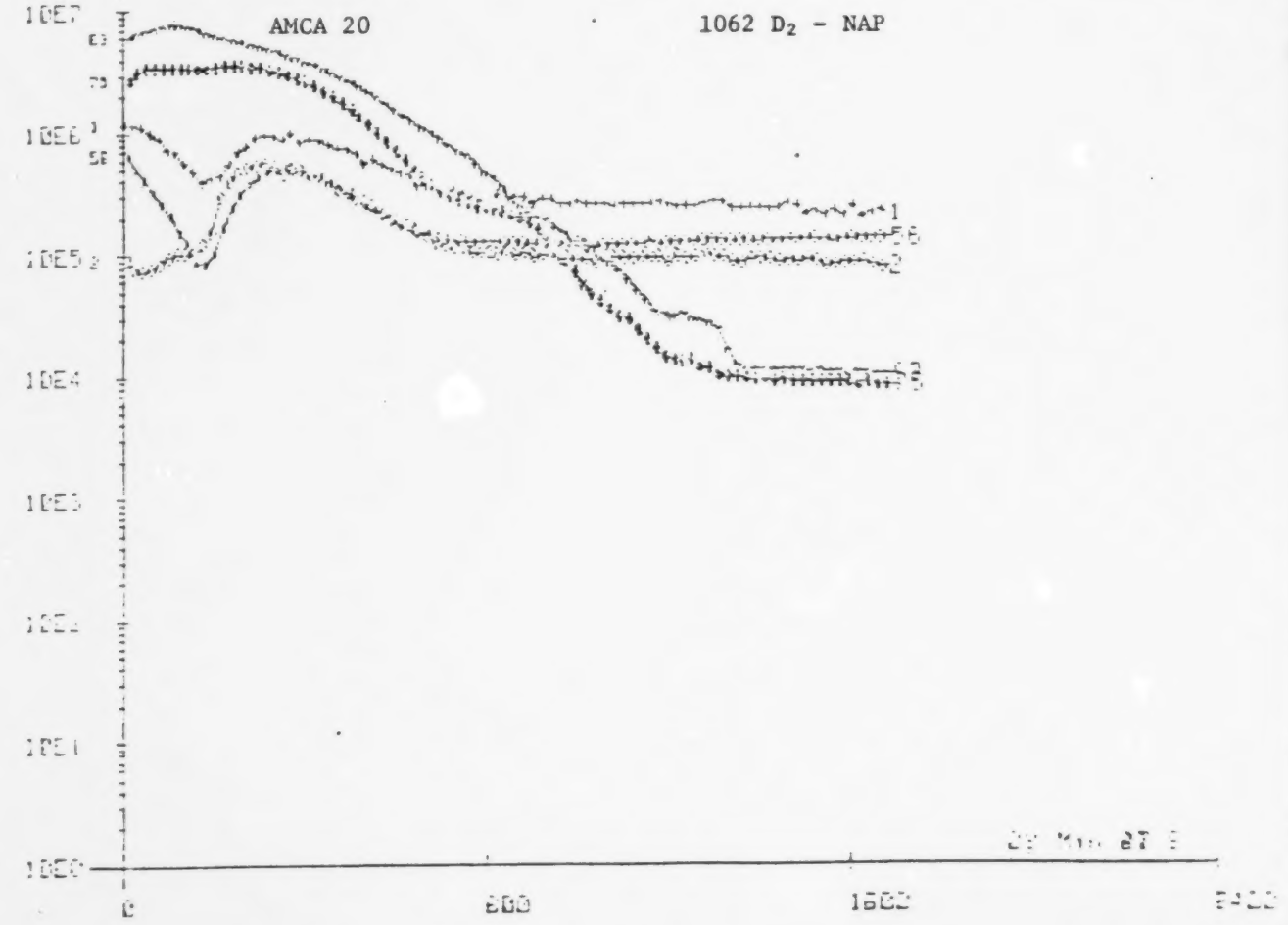
Appendix III: i) SIMS depth profiles of deuterium charged AISI 1062, 4037 and 4140 steels with and without NAP treatment. x-axis: Time/s; y-axis: Intensity/Counts per Second

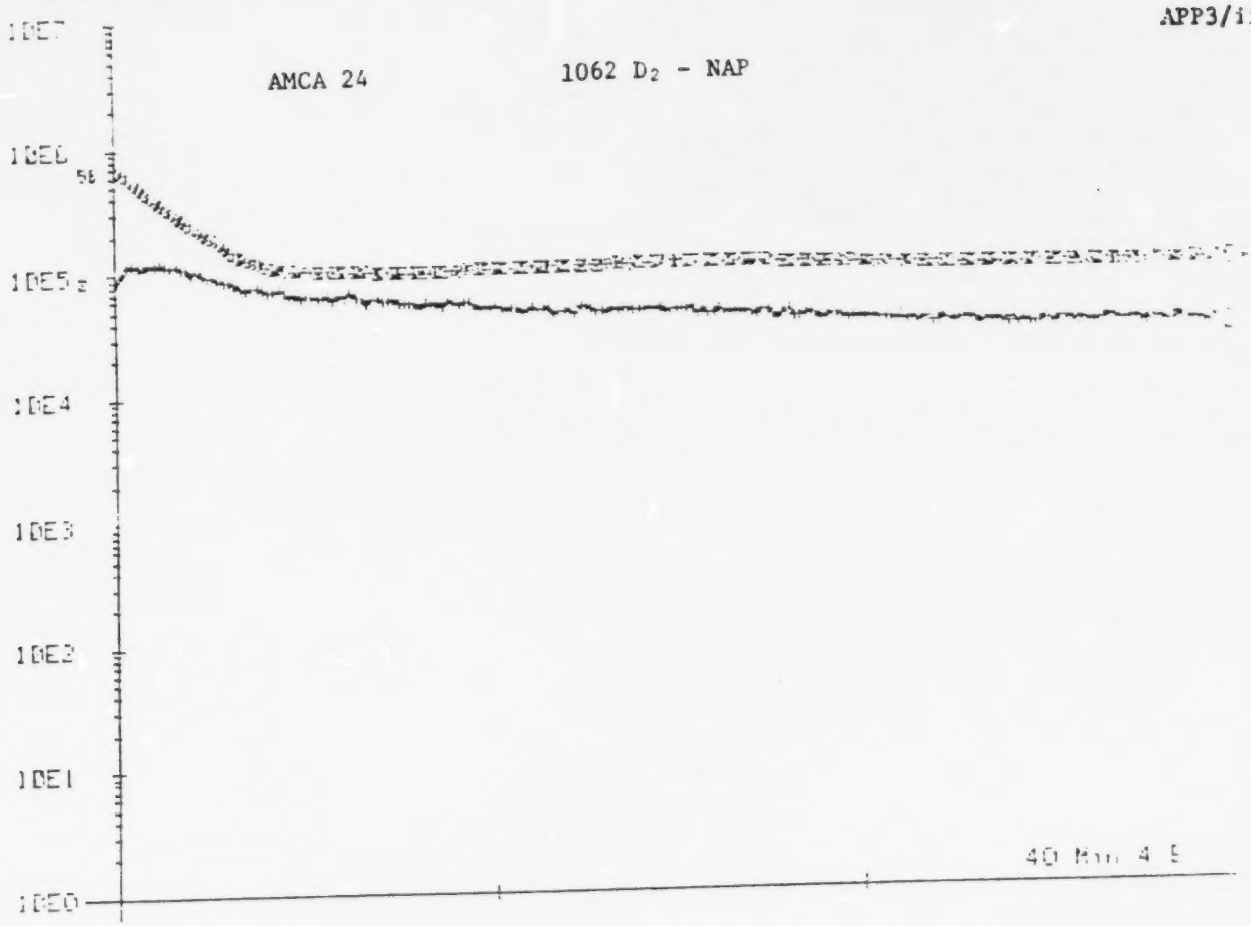
ii) Table 1: Iron, hydrogen, deuterium and copper secondary ion signal intensities in deuterium charged AISI 1062, 4037 and 4140 steels.

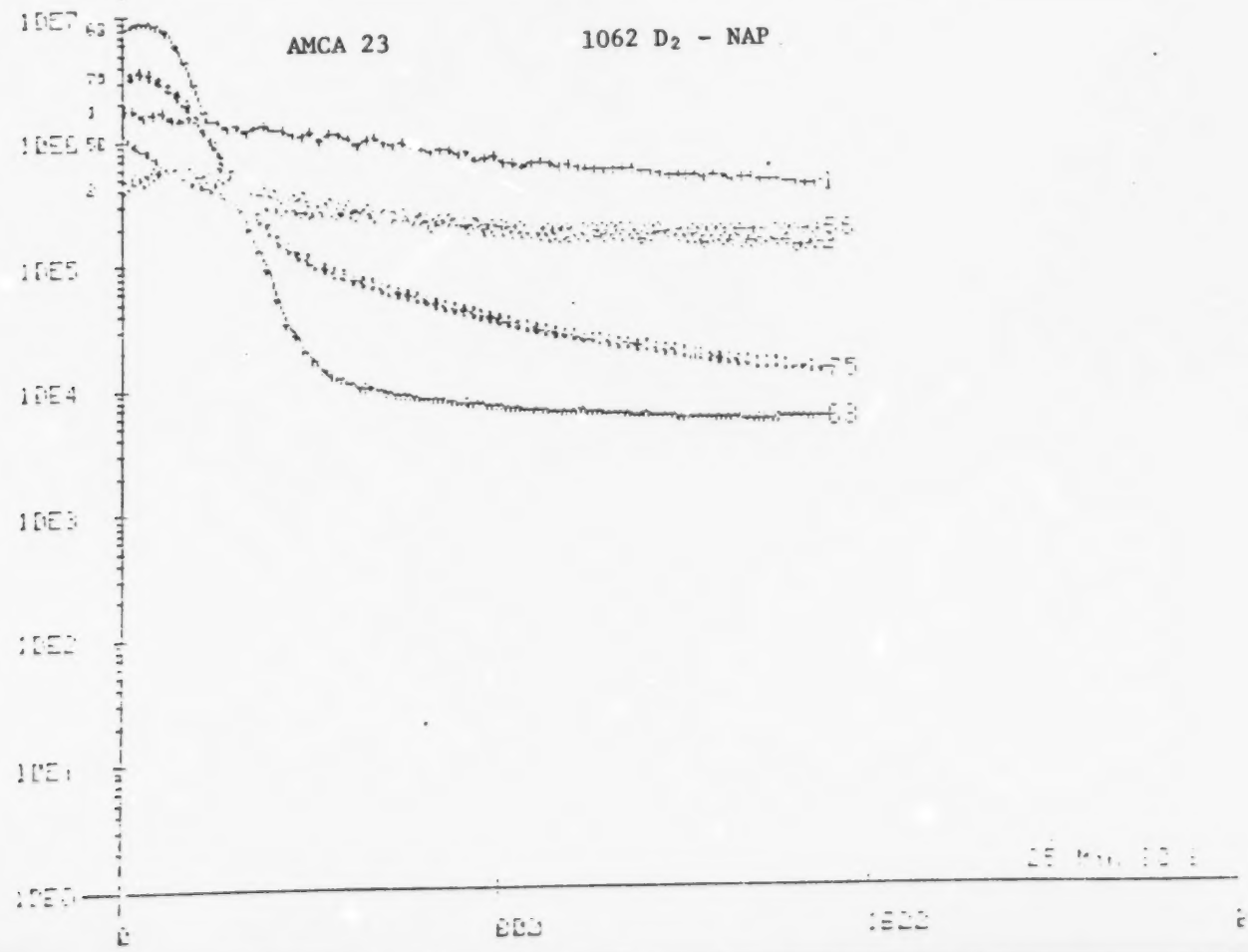

AMCA 21
1062 D_2
1DE5
1DE4
1DE3
1DE2
1DE1
1DE0
39 Min 10 S

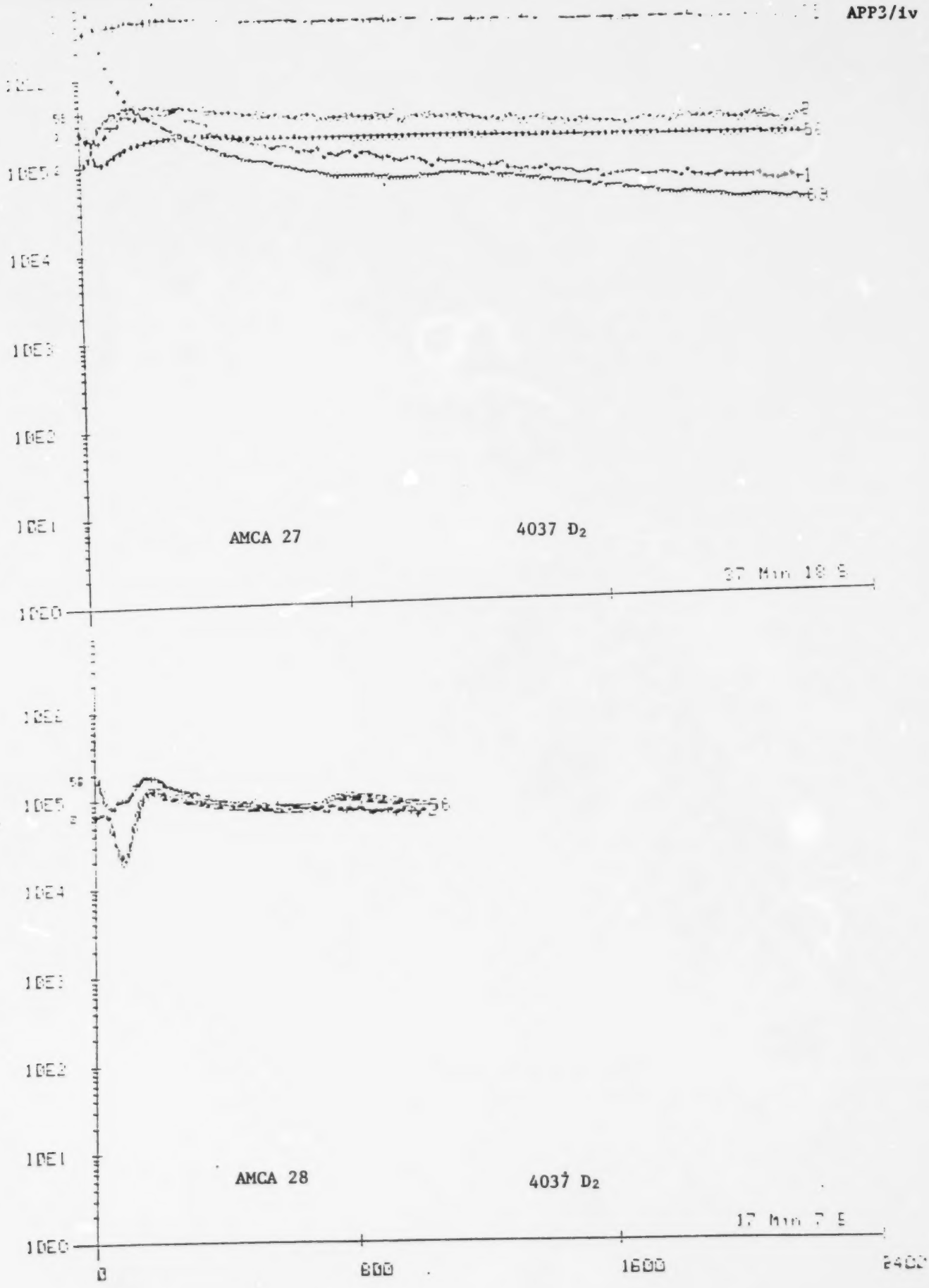

AMCA 22
1062 D_2
1DE7
1DE6
1DE5
1DE4
1DE2
1DE1
1DE0
29 Min 5 S
800
1600

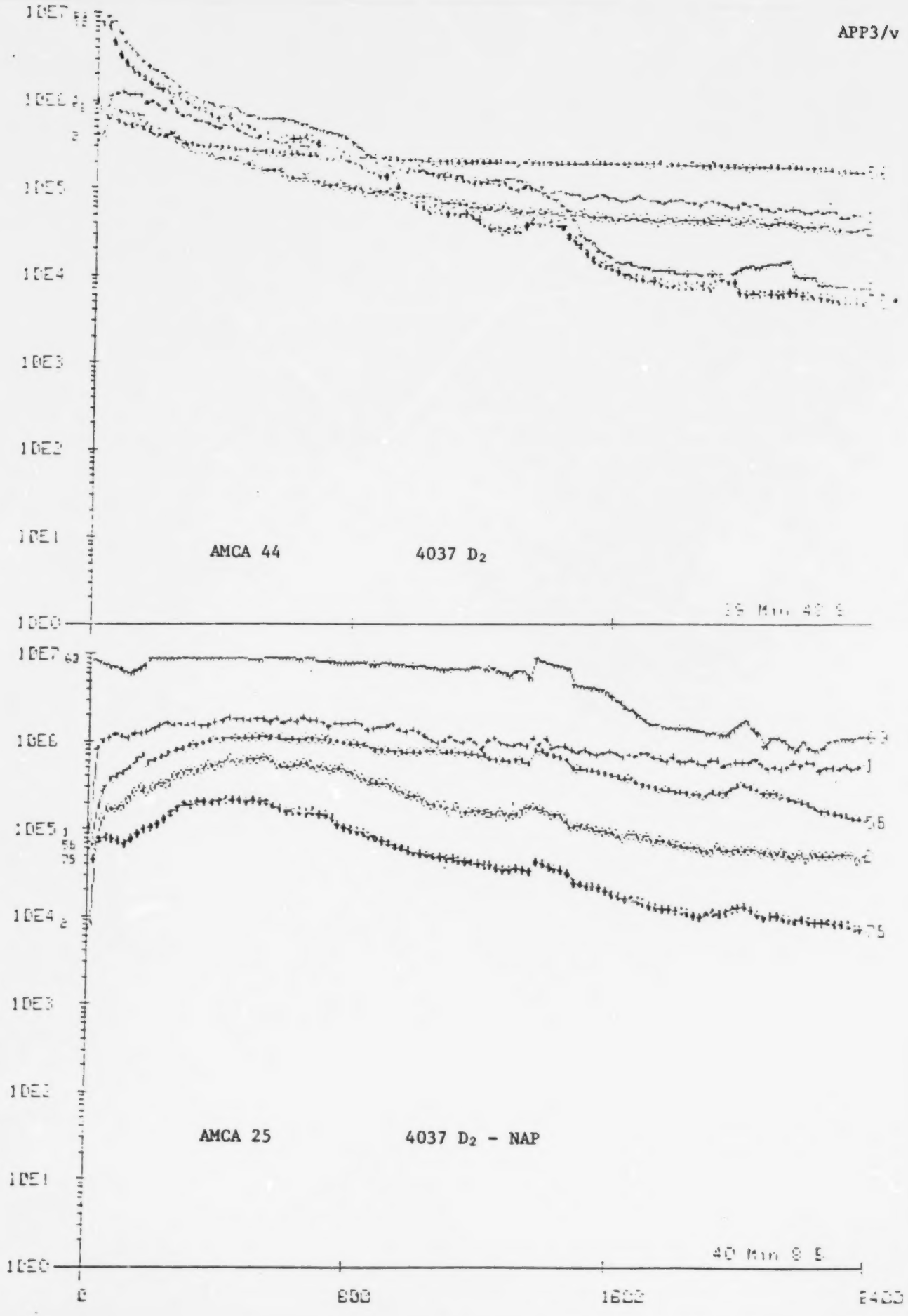

AMCA 1B
1062 D_2
10E6
10E5
10E4
10E3
10E2
10E1
10E0
3 Min 33 5

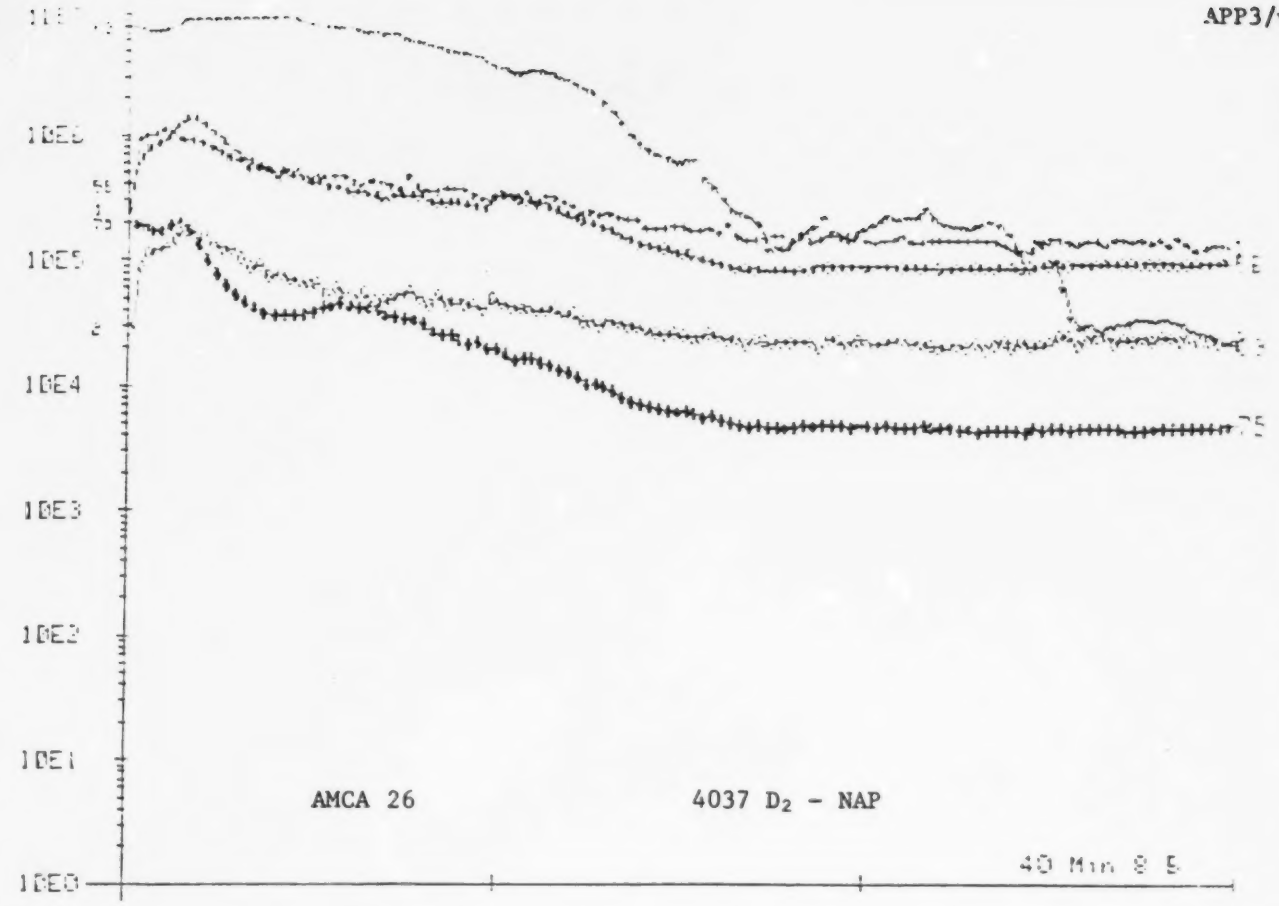

AMCA 20
1062 D_2 - NAP
10E6
10E5
10E4
10E3
10E2
10E1
10E0
800
1600

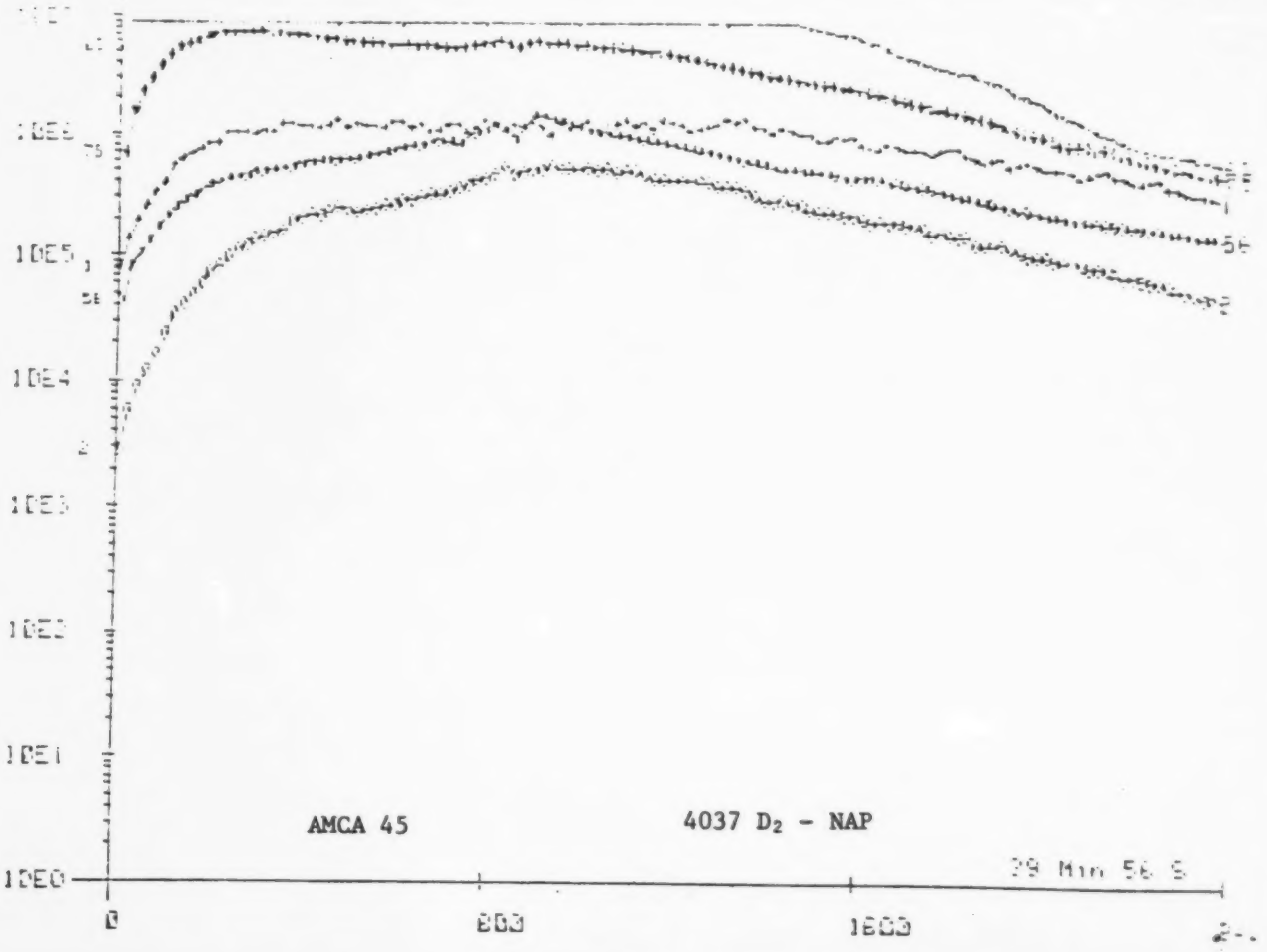

AMCA 24
1062 D2 - NAP
10E7
10E6
10E5
10E4
10E3
10E2
10E1
10E0
40 Min 4 S

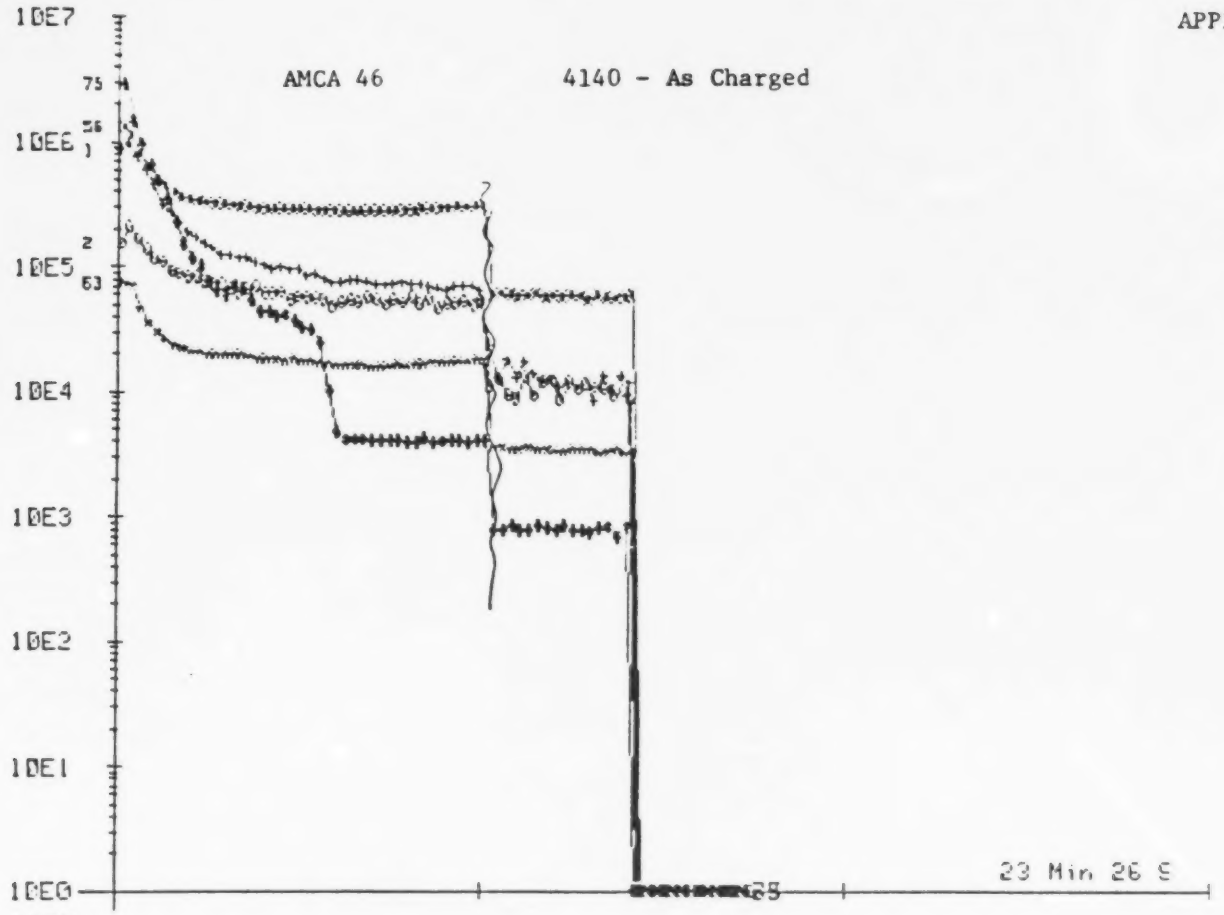

AMCA 23
1062 D2 - NAP
10E7
10E6
10E5
10E4
10E3
10E2
10E1
10E0
0
800
1600

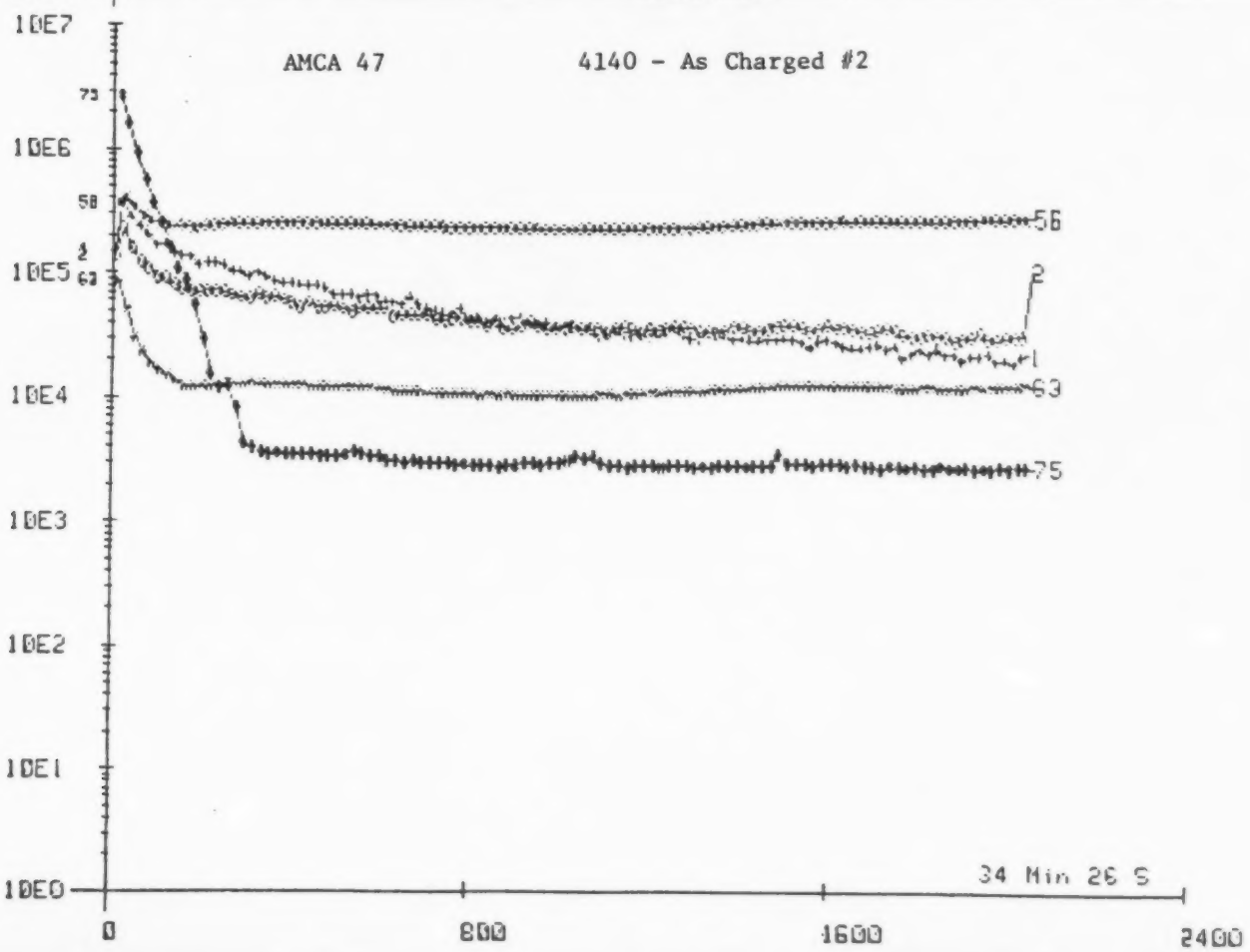

AMCA 27
4037 D2
37 Min 18 S
AMCA 28
4037 D2
17 Min 7 S
0
800
1600
2400

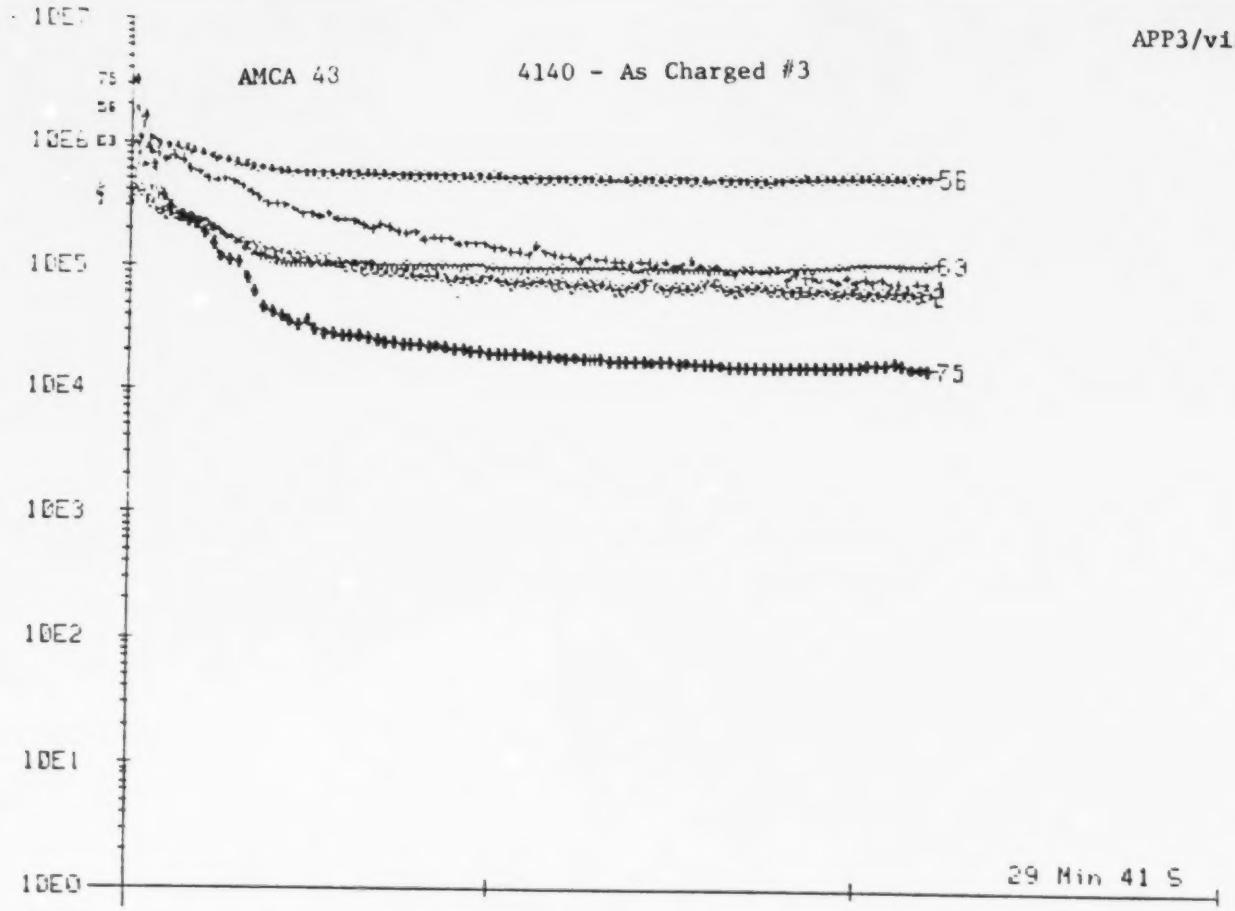

AMCA 44
4037 D2
AMCA 25
4037 D2 - NAP
40 Min 0 S
0
800
1600
2400

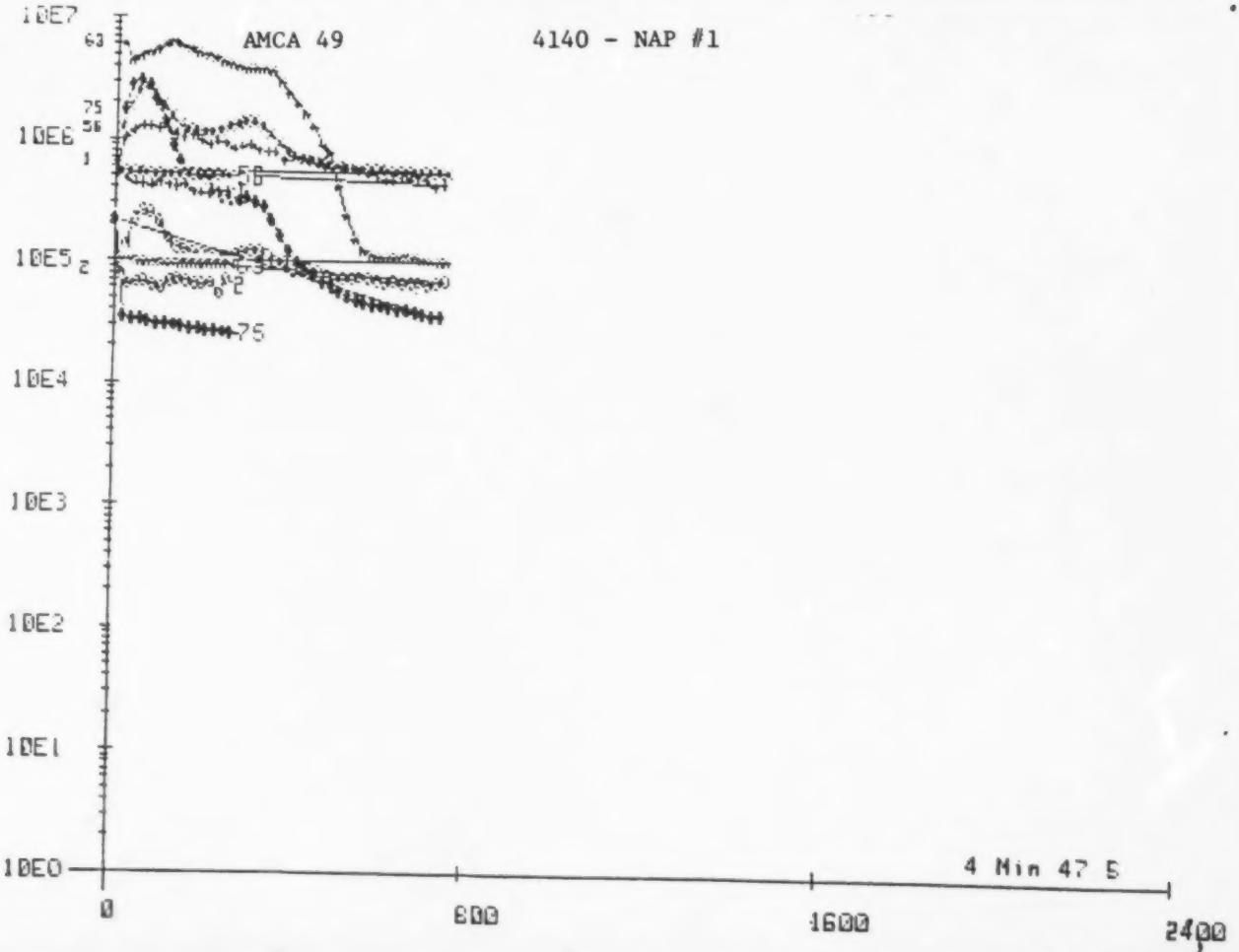

10E6
10E5
10E4
10E3
10E2
10E1
10E0
AMCA 26
4037 D2 - NAP
40 Min 0 S

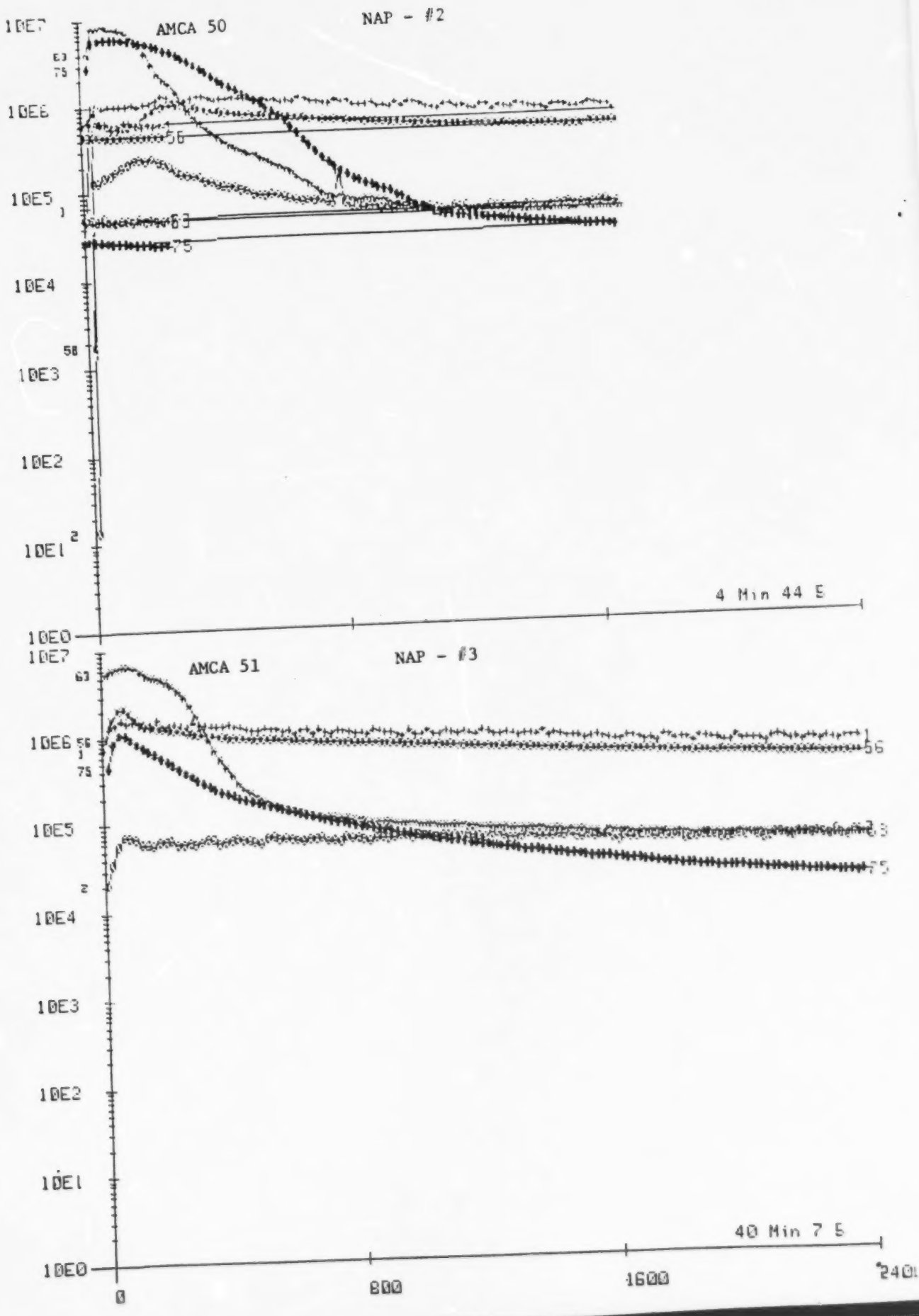

10E5
10E4
10E3
10E2
10E1
10E0
AMCA 45
4037 D2 - NAP
29 Min 56 S
0
800
1600


AMCA 46
4140 - As Charged
10E7
10E6
10E5
10E4
10E3
10E2
10E1
10E0
75
56
2
63
23 Min 26 S


AMCA 47
4140 - As Charged #2
10E7
10E6
10E5
10E4
10E3
10E2
10E1
10E0
75
58
2
63
56
2
1
63
75
34 Min 26 S
0
800
1600
2400


AMCA 43
4140 - As Charged #3
10E7
10E6
10E5
10E4
10E3
10E2
10E1
10E0
56
63
75
29 Min 41 S


AMCA 49
4140 - NAP #1
10E7
10E6
10E5
10E4
10E3
10E2
10E1
10E0
63
75
56
1
2
0
4 Min 47 S
0
800
1600
2400


AMCA 50
NAP - #2
10E7
10E6
10E5
10E4
10E3
10E2
10E1
10E0
63
75
56
4 Min 44 S
AMCA 51
NAP - #3
40 Min 7 S
0
800
1600
2401

APPENDIX III: TABLE 1

IRON, HYDROGEN, DEUTERIUM AND COPPER SECONDARY ION SIGNAL INTENSITIES IN DEUTERIUM CHARGED AISI 1062, 4037 AND 4140 STEELS

I = Initial Signal; F = Final Signal

Steel	Condition	Secondary Ion $^{56}Fe^-$ I	$^{56}Fe^-$ F	$^{1}H^-$ I	$^{1}H^-$ F	$^{2}D^-$ I	$^{2}D^-$ F	$^{63}Cu^-$ I	$^{63}Cu^-$ F	Initial Time, s	Final Time, s
		x10^5		x10^5		x10^5		x10^5			
1062	Charged										
	Sample 1	5.84	1.50	4.40	1.51	1.61	1.21	17.60	0.057	7	1890
	Sample 2	8.48	1.91	---	--	3.14	1.11	---	---		1745
	Sample 3	0.95	0.91	0.70	0.11	1.03	0.10	49.60	0.280		
1062	Charged + NAP Treated										
	Sample 1	6.57	1.34	11.91	2.09	0.91	0.78	61.20	0.100	6	1721
	Sample 2	10.08	1.87	18.14	4.40	4.31	1.43	83.68	0.057	7	1530
	Sample 3	6.73	0.99	---	--	0.89	0.30	---	---	6	2404
4037	Charged										
	Sample 1	4.03	1.63	2.46	0.49	1.02	2.84	61.28	0.290	6	2238
	Sample 2	1.79	0.84	---	--	0.66	0.73	---	---	6	1027
	Sample 3	8.18	1.56	10.09	0.48	3.87	0.35	88.00	0.071	6	2388

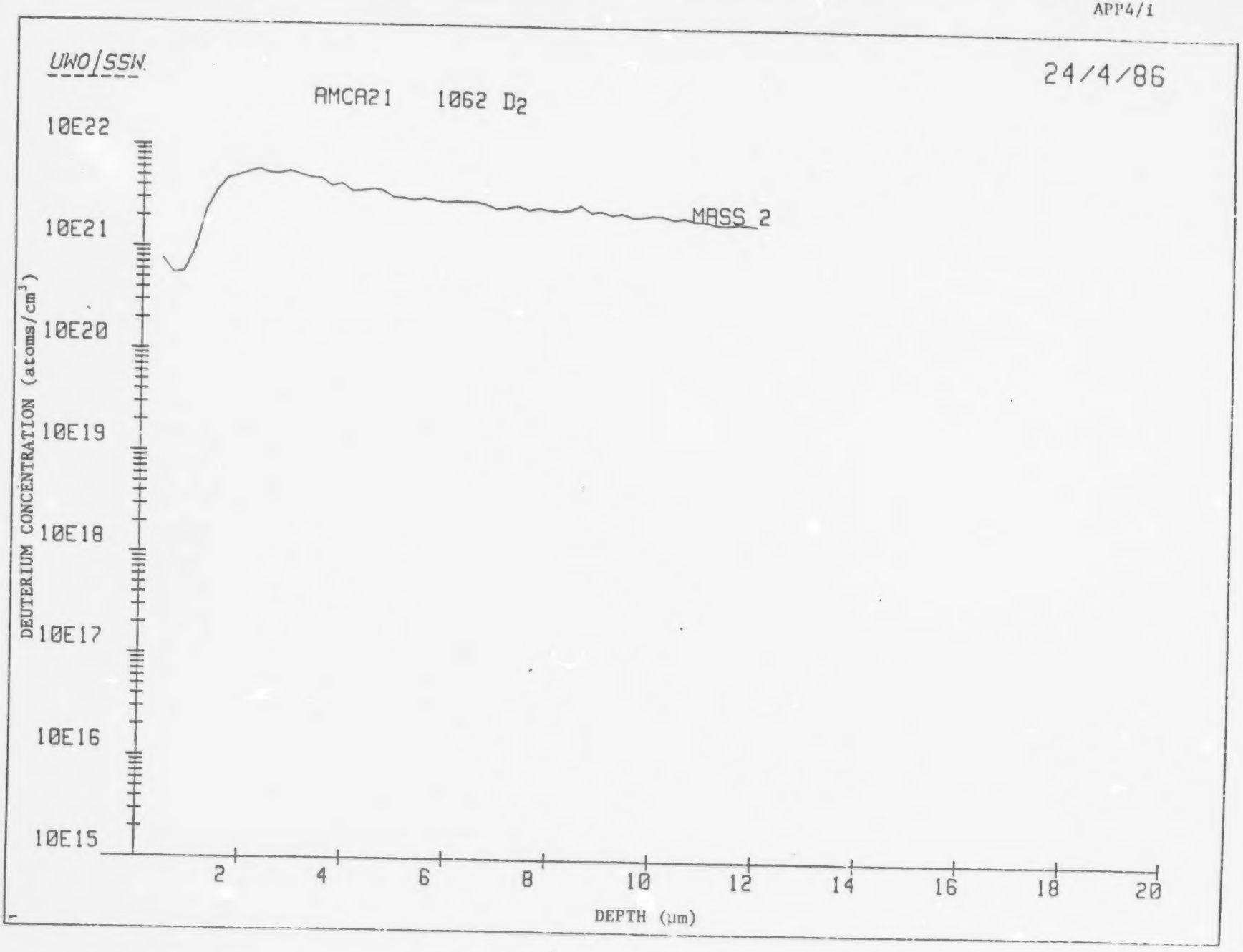
.../continued

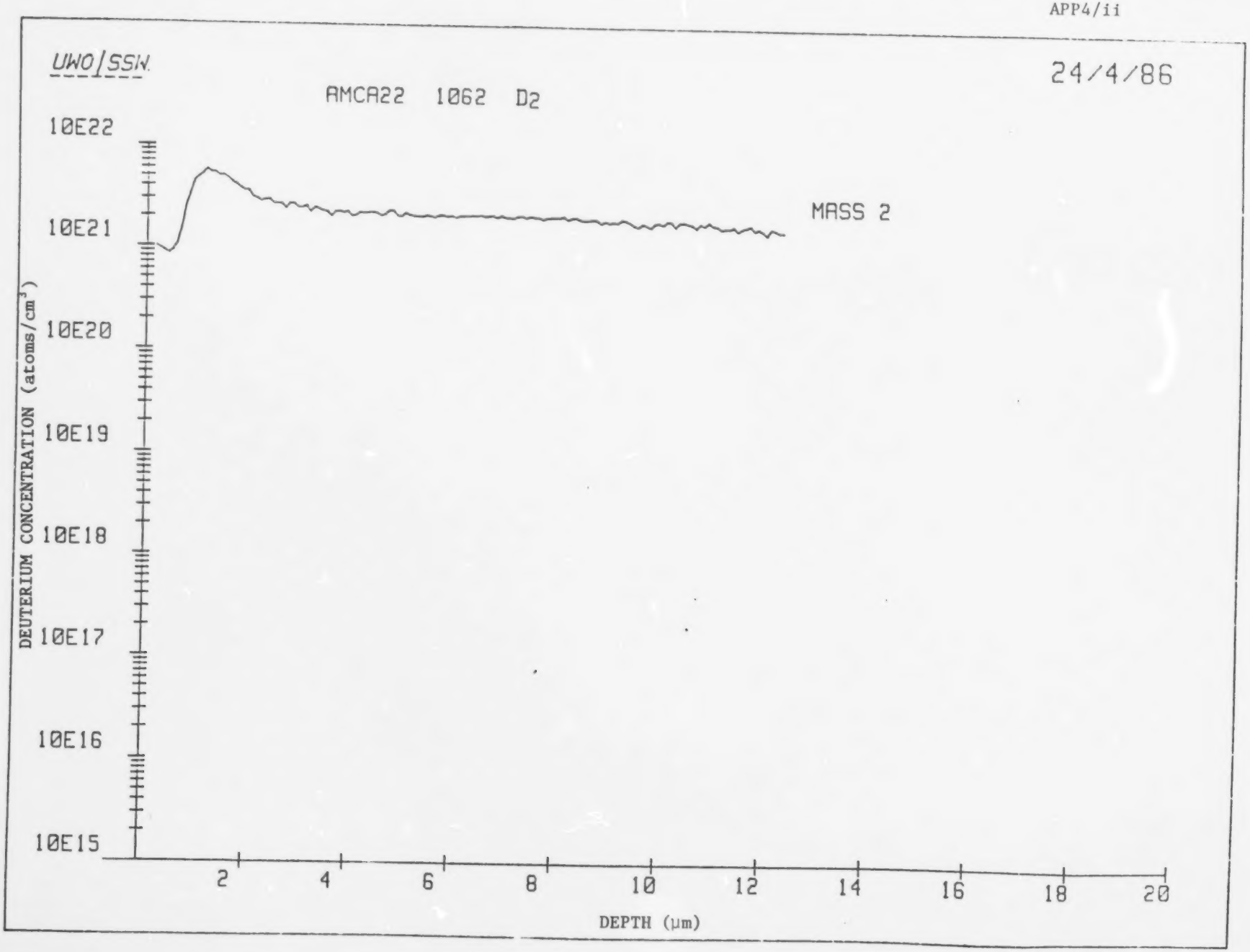
APPENDIX III: TABLE 1...continued

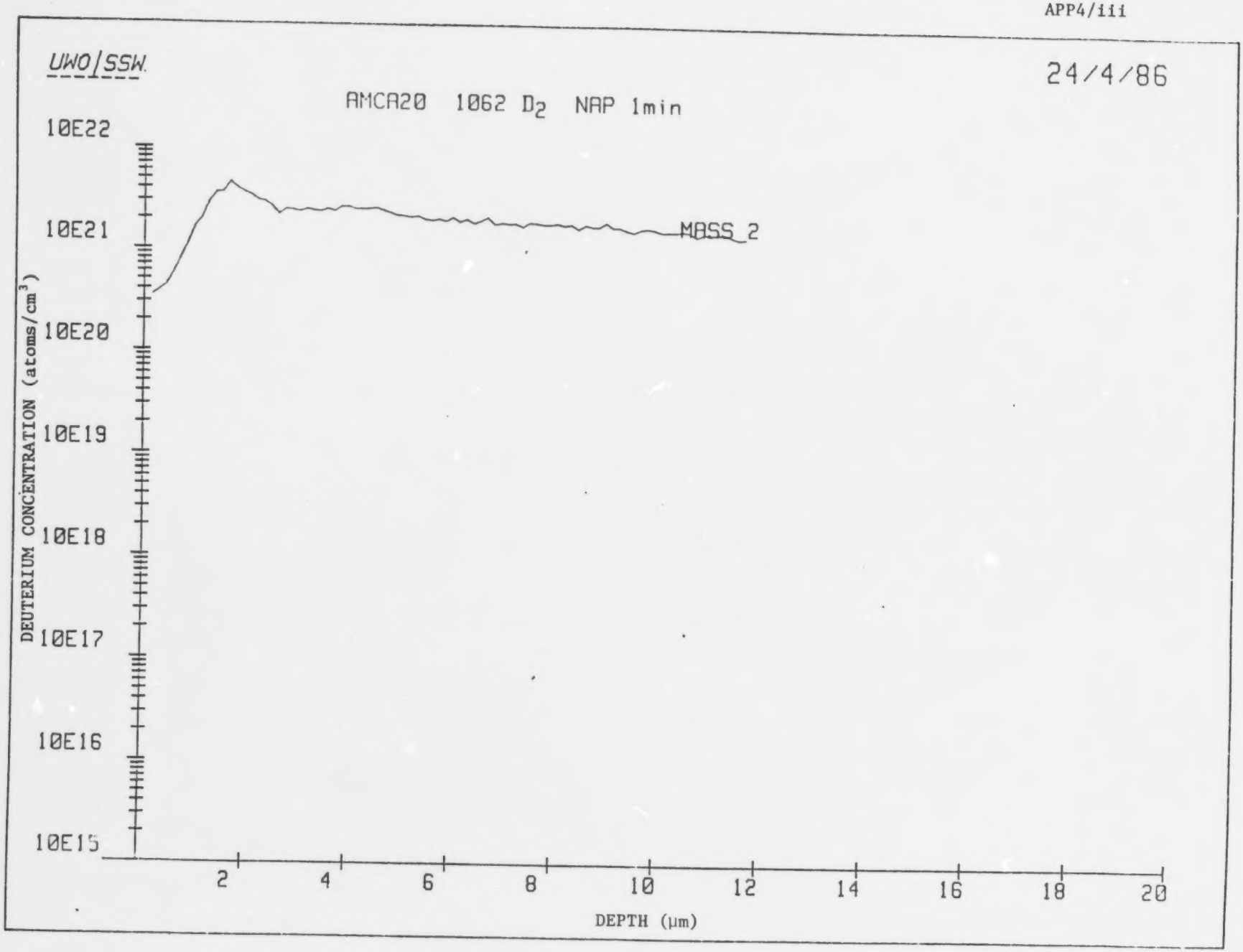
Steel	Condition	Secondary Ion $^{56}Fe^-$ I	$^{56}Fe^-$ F	$^{1}H^-$ I	$^{1}H^-$ F	$^{2}D^-$ I	$^{2}D^-$ F	$^{63}Cu^-$ I	$^{63}Cu^-$ F	Initial Time, s	Final Time, s
4037	Charged + NAP Treated - 3 min	x10^5		x10^5		x10^5		x10^5			
	Sample 1	0.66	1.28	0.91	5.72	0.082	1.280	87.32	11.99	7	2408
	Sample 2	3.89	0.98	2.53	1.30	0.280	0.229	77.11	0.21	7	2408
	Sample 3	0.43	1.51	0.81	3.18	0.028	0.490	54.11	5.90	6	
4140	Charged										
	Sample 1	13.30	3.04	8.68	0.12	1.540	0.120	0.74	1.75	6	806
	Sample 2	3.69	2.89	1.48	0.22	1.370	0.320	0.87	0.13	8	2042
	Sample 3	18.67	5.50	3.43	0.70	4.000	0.610	9.90	1.05	6	1780
	Charged + NAP Treated - 3 min										
	Sample 1	12.30	0.91	6.61	4.49	0.850	0.670	62.06	1.01	6	740
	Sample 2	7.03	4.50	10.08	7.05	1.310	0.510	41.64	0.47	30	1680
	Sample 3	9.69	4.32	6.26	6.00	0.210	0.520	56.82	0.49	6	2403

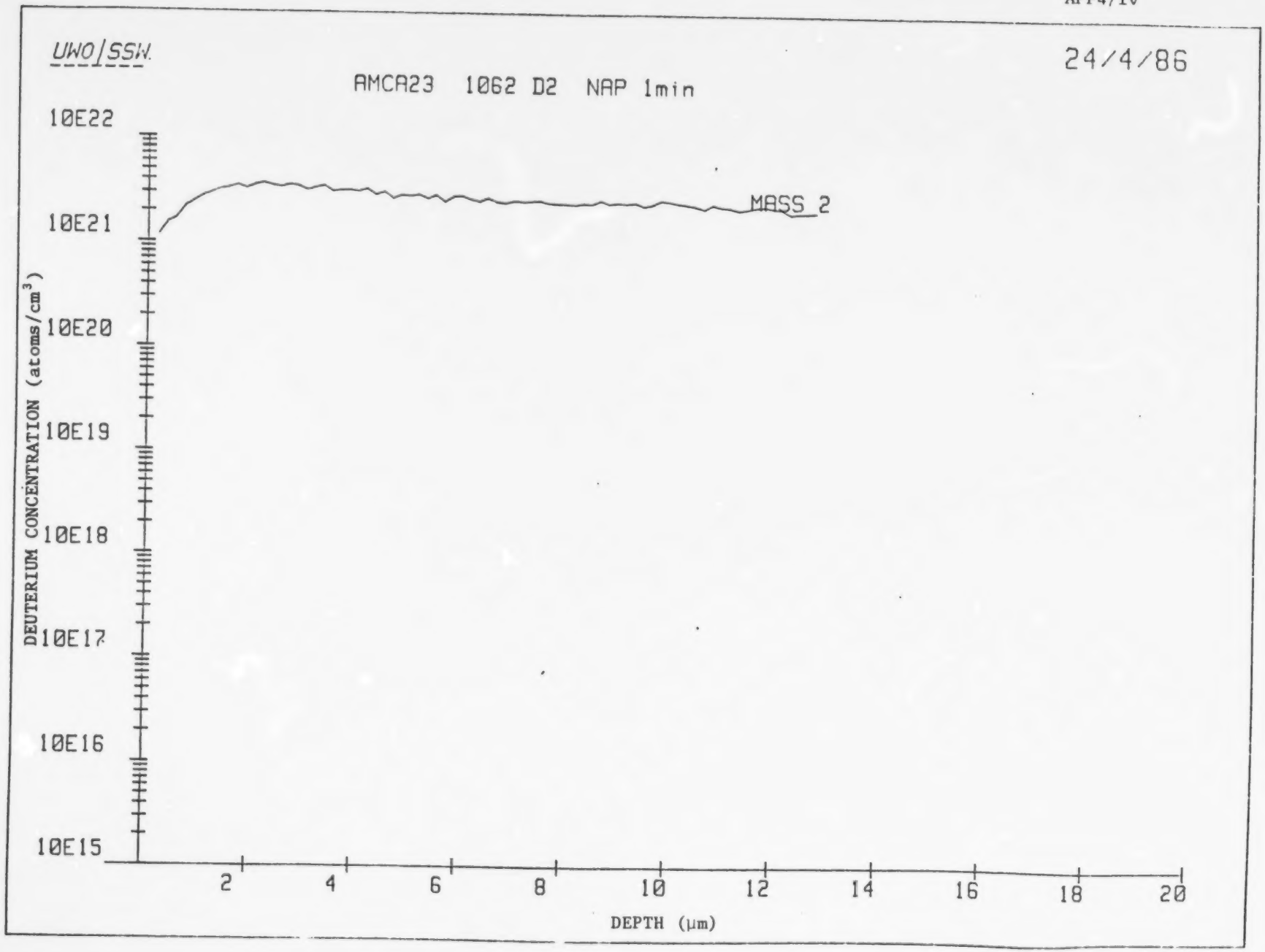
Appendix IV: Deuterium concentration vs sputtered depth profiles of 1062, 4037 and 4140 steels with and without NAP treatment.

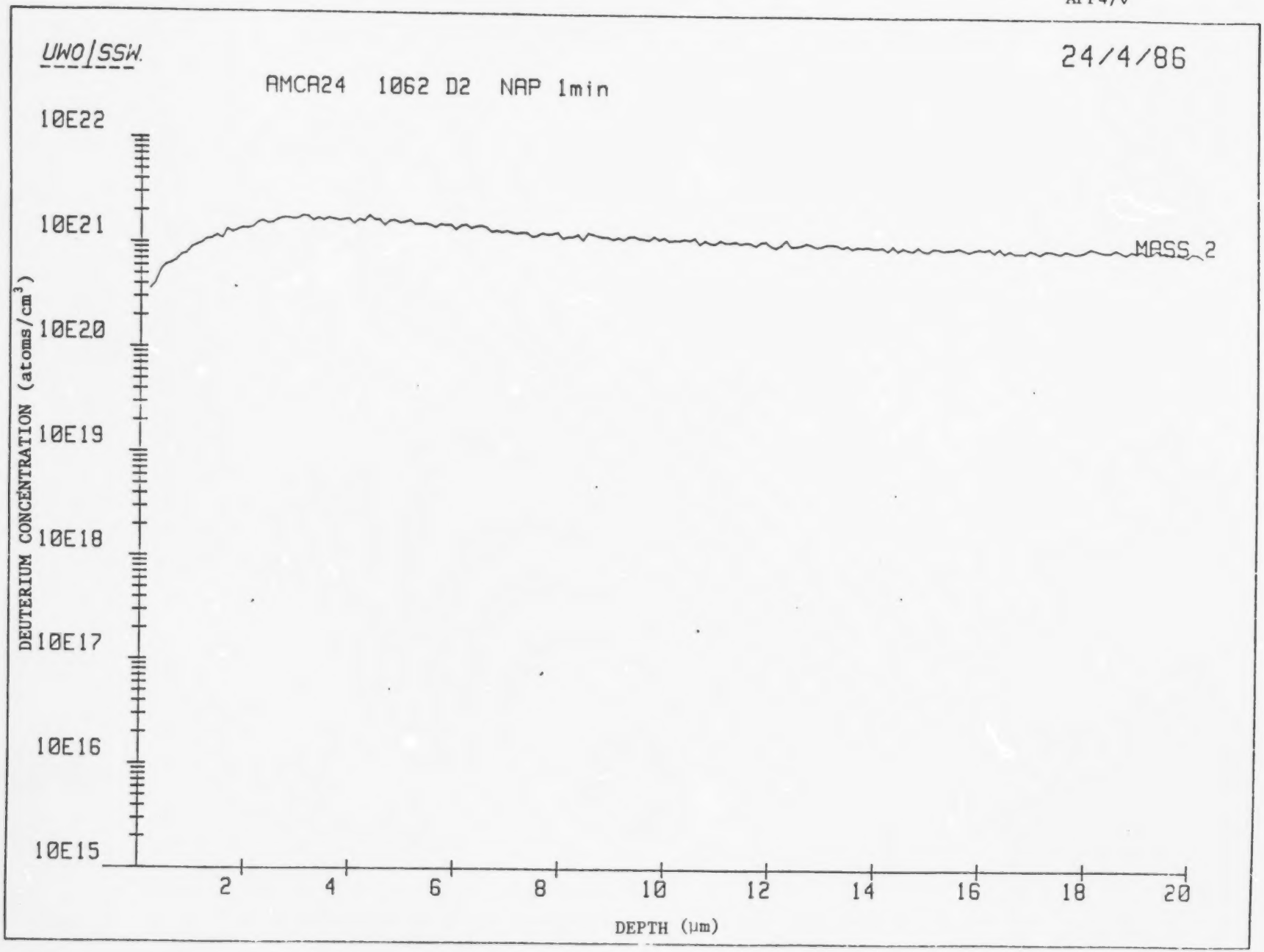
x-axis - Depth (μm)
y-axis - Deuterium Concentration (atoms/cm^3)

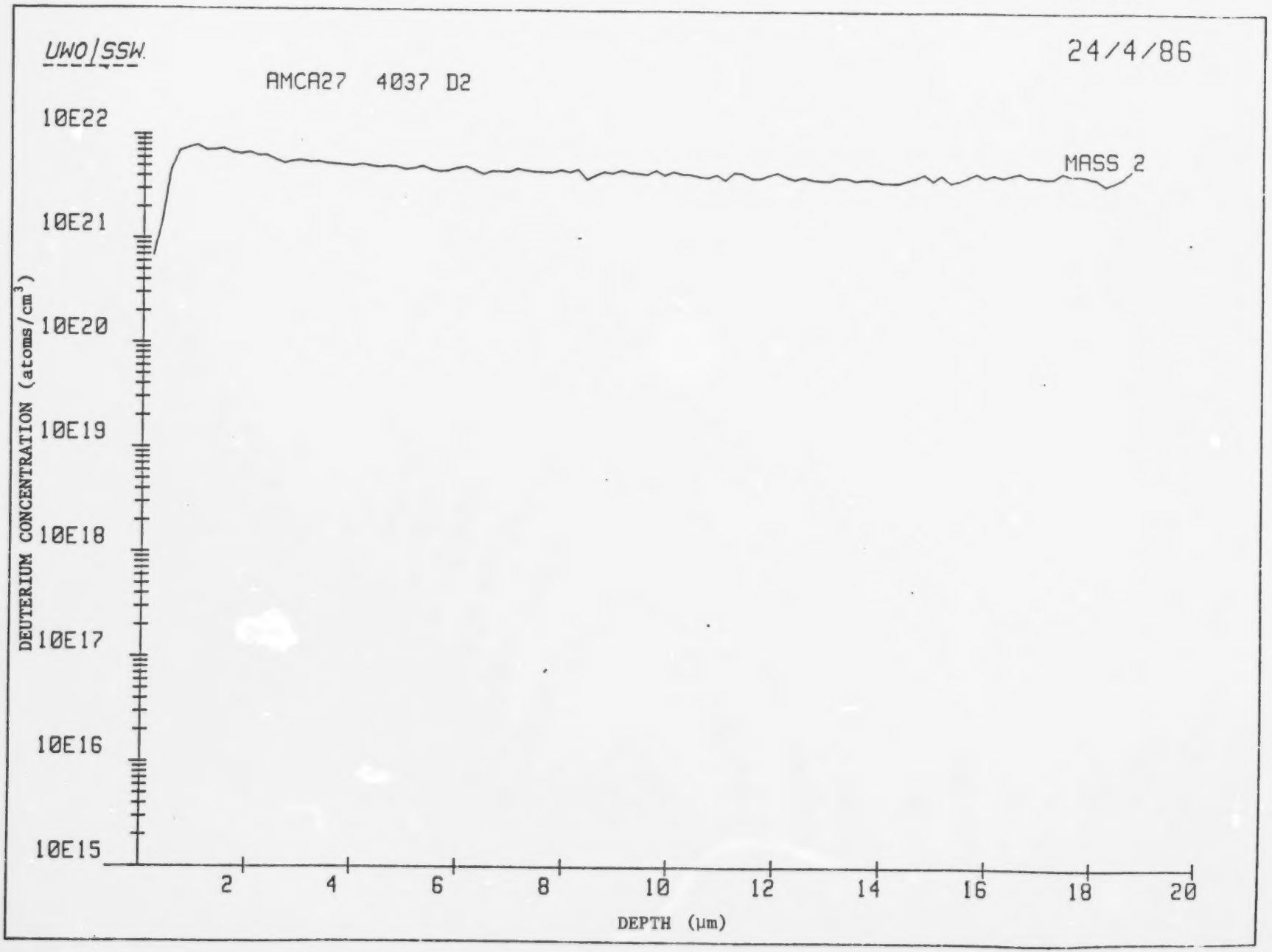

UWO/SSW
24/4/86
AMCA21 1062 D_2
MASS 2
10E22
10E21
10E20
10E19
10E18
10E17
10E16
10E15
DEUTERIUM CONCENTRATION (atoms/cm^3)
2
4
6
8
10
12
14
16
18
20
DEPTH (μm)

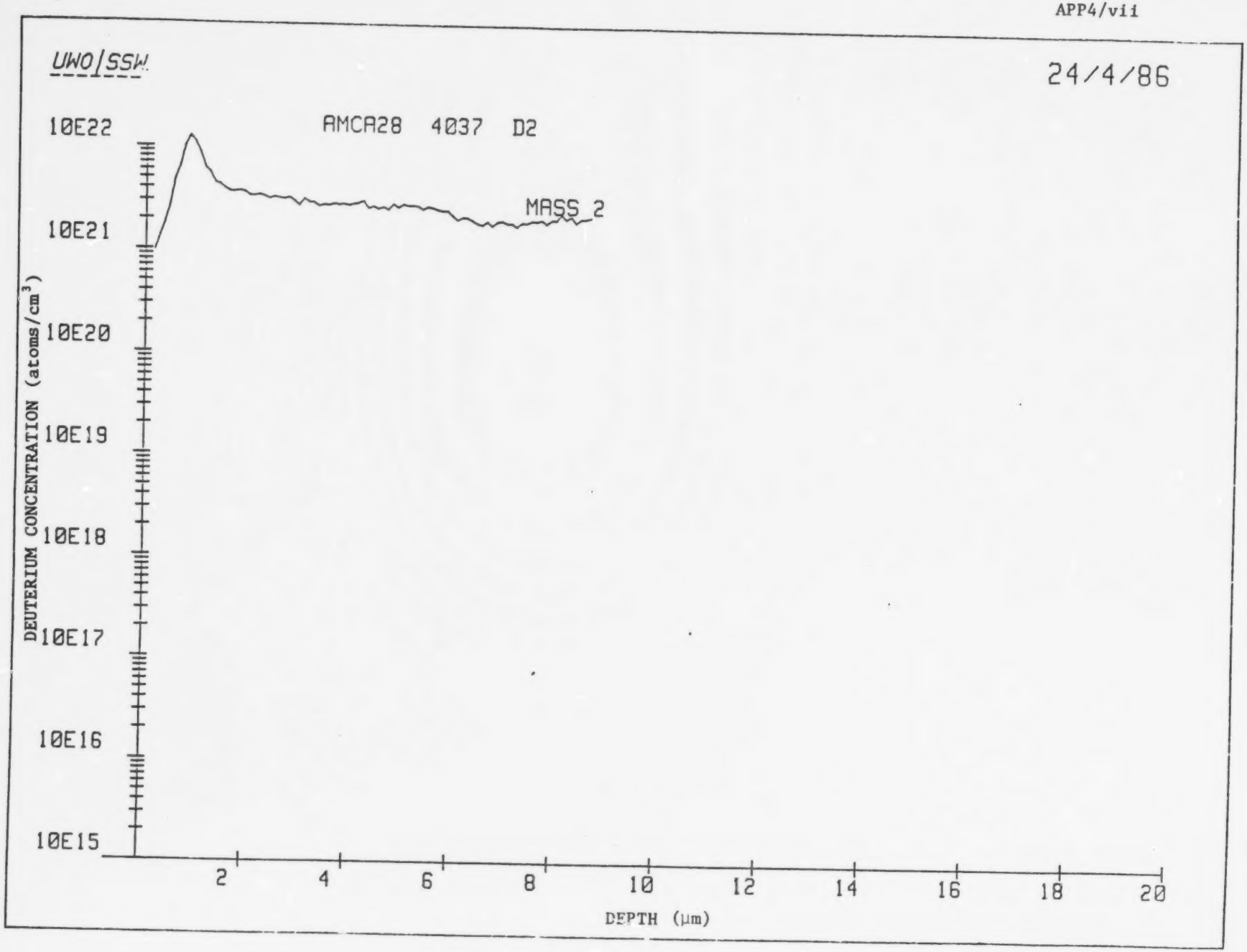

UWO/SSW
24/4/86
AMCA22 1062 D2
MASS 2
DEUTERIUM CONCENTRATION (atoms/cm³)
10E22
10E21
10E20
10E19
10E18
10E17
10E16
10E15
2
4
6
8
10
12
14
16
18
20
DEPTH (μm)

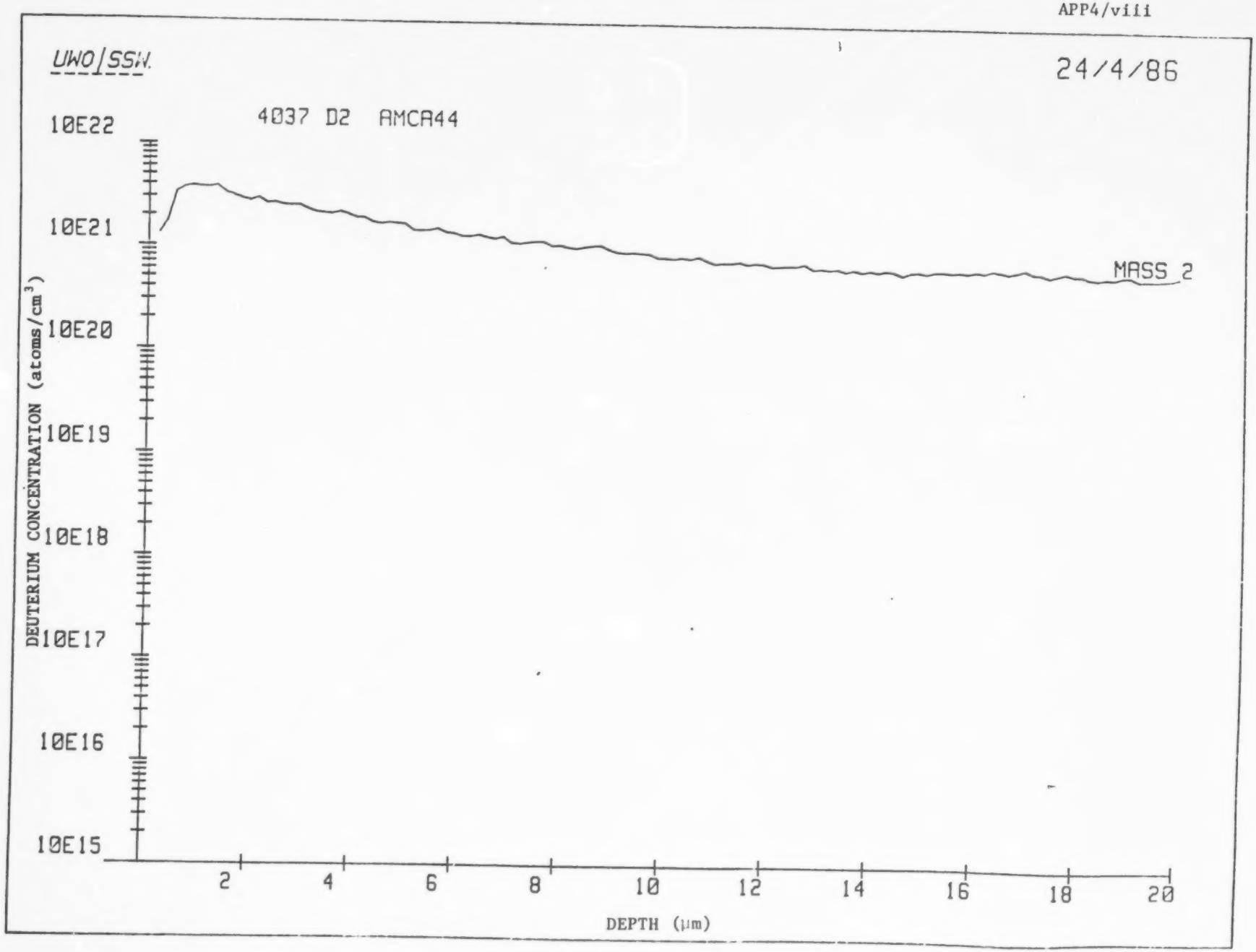

UWO/SSW
24/4/86
AMCA20 1062 D_2 NAP 1min
MASS 2
10E22
10E21
10E20
10E19
10E18
10E17
10E16
10E15
DEUTERIUM CONCENTRATION (atoms/cm^3)
2
4
6
8
10
12
14
16
18
20
DEPTH (μm)

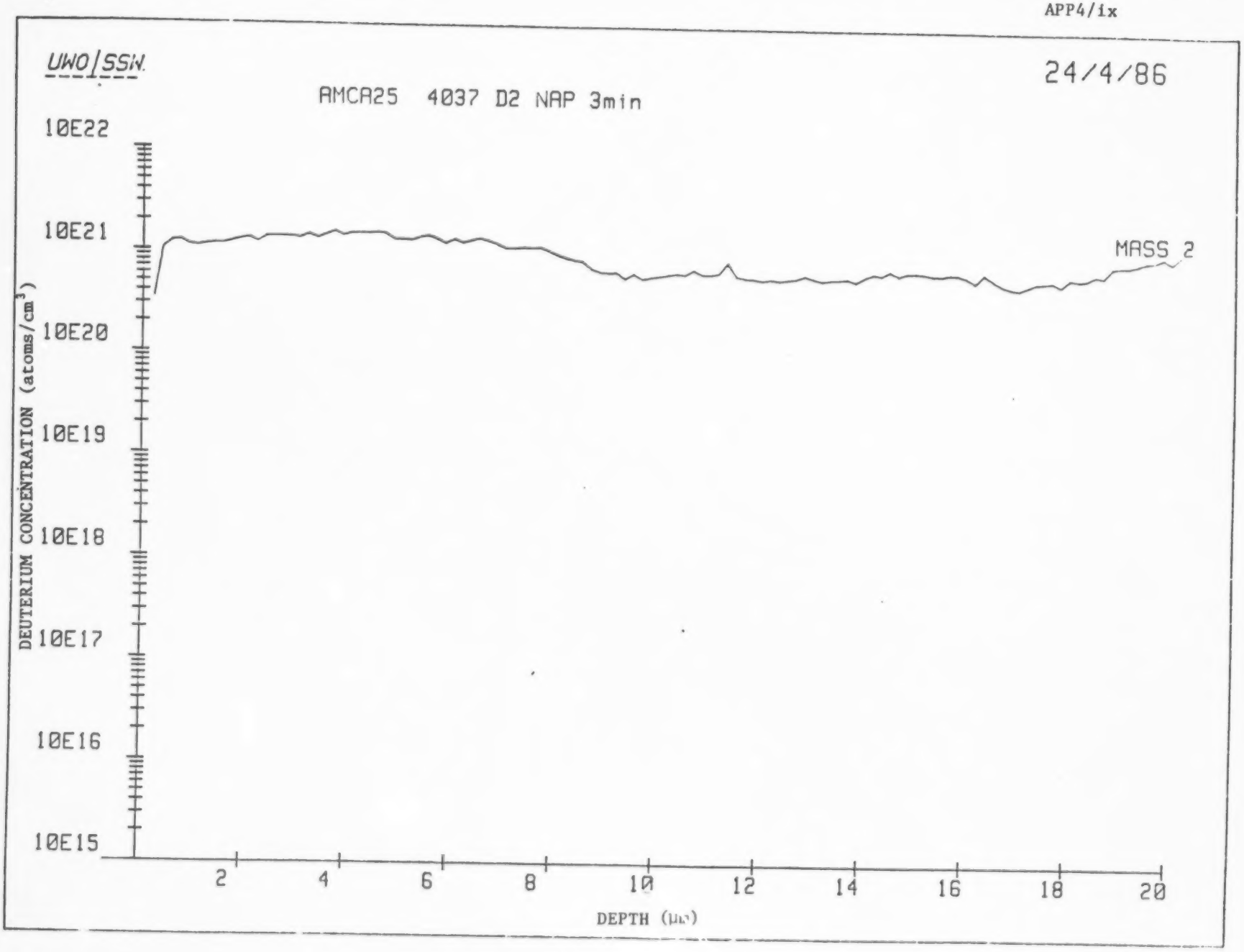

UWO/SSW
24/4/86
AMCA23 1062 D2 NAP 1min
MASS 2
DEUTERIUM CONCENTRATION (atoms/cm^3)
10E22
10E21
10E20
10E19
10E18
10E17
10E16
10E15
2
4
6
8
10
12
14
16
18
20
DEPTH (μm)

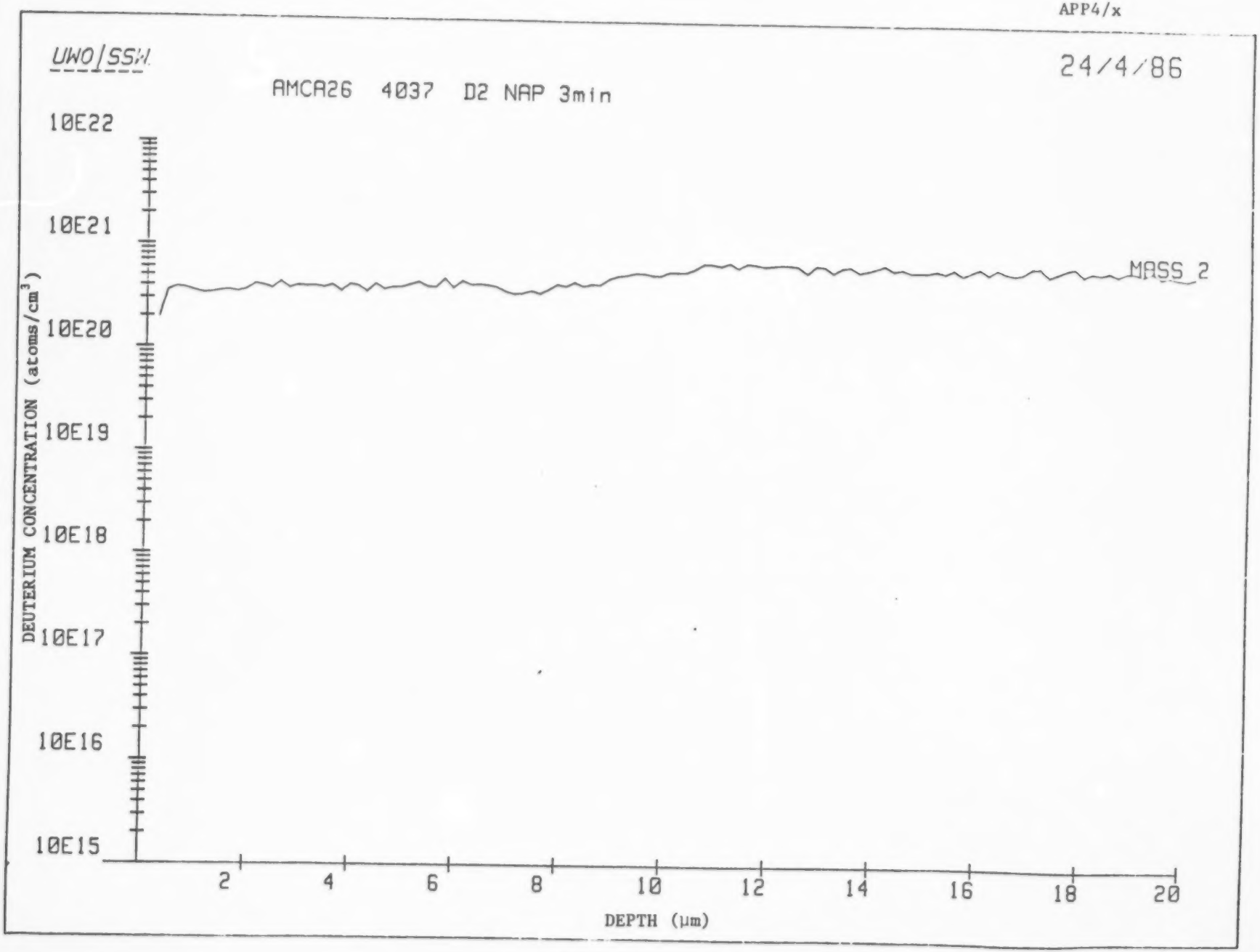

UWO/SSW
24/4/86
AMCA24 1062 D2 NAP 1min
10E22
10E21
10E20
10E19
10E18
10E17
10E16
10E15
DEUTERIUM CONCENTRATION (atoms/cm³)
MASS 2
2
4
6
8
10
12
14
16
18
20
DEPTH (µm)

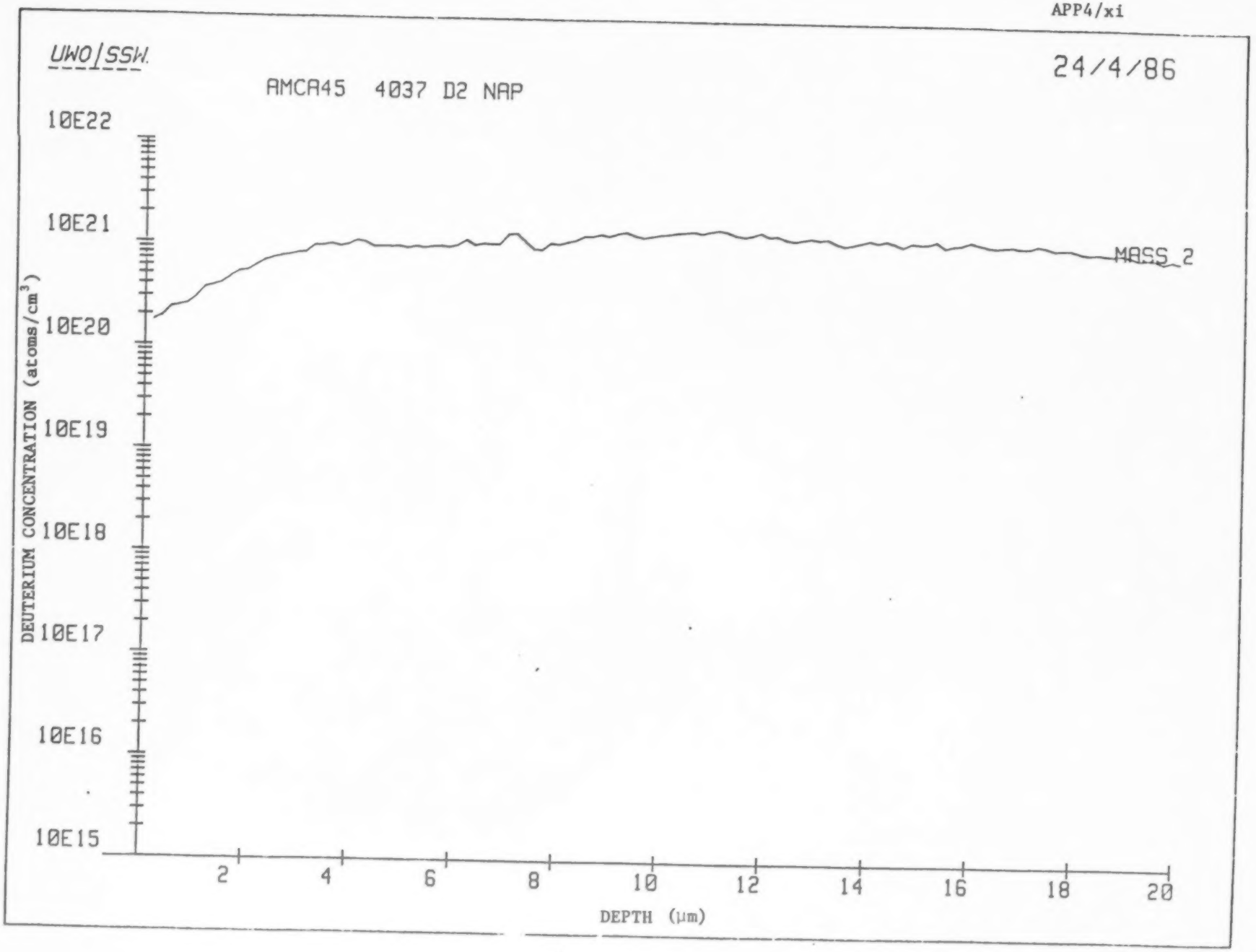

UWO/SSW
24/4/86
AMCA27 4037 D2
MASS 2
10E22
10E21
10E20
10E19
10E18
10E17
10E16
10E15
DEUTERIUM CONCENTRATION (atoms/cm3)
2
4
6
8
10
12
14
16
18
20
DEPTH (µm)

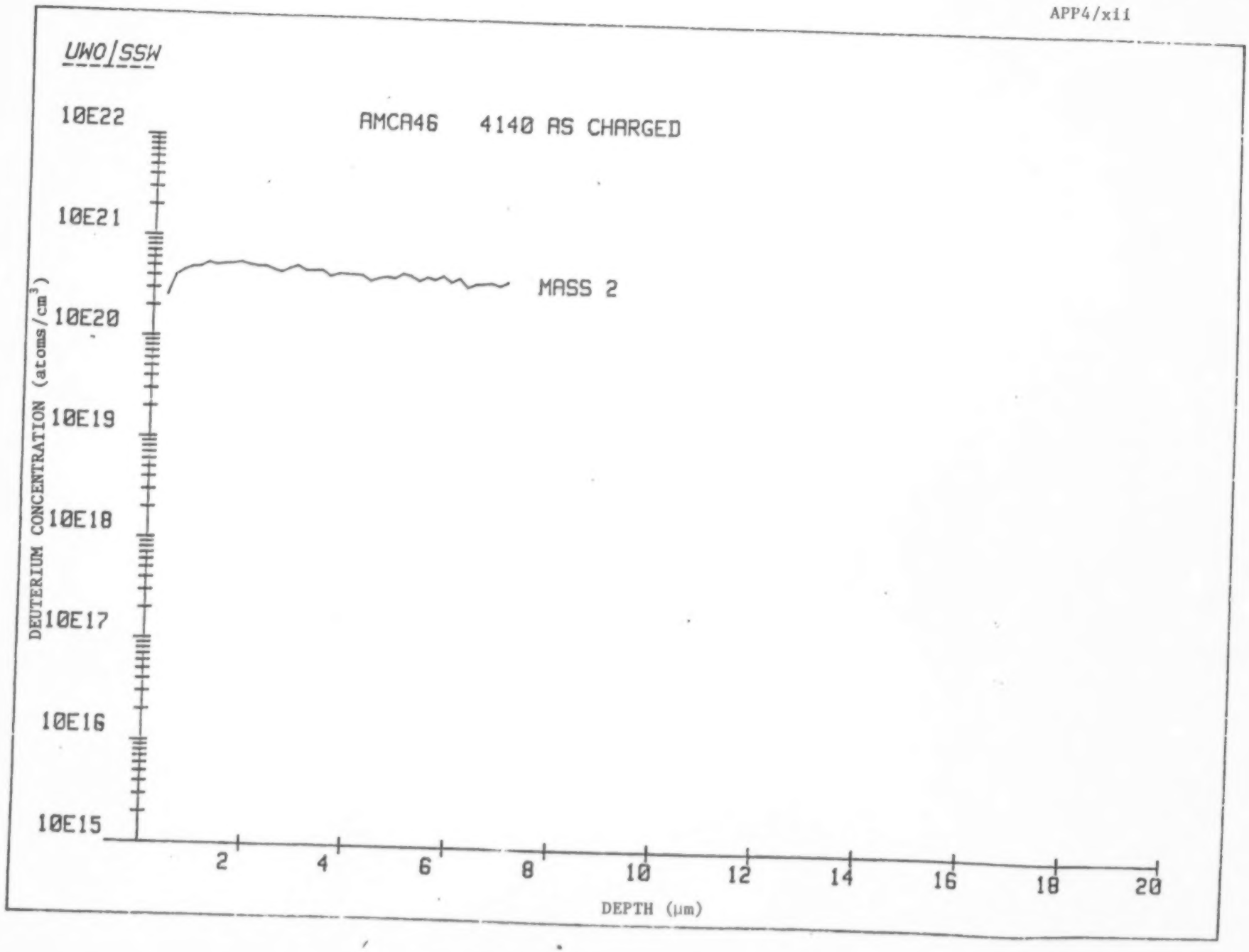

UWO/SSW
24/4/86
AMCA28 4037 D2
MASS 2
10E22
10E21
10E20
10E19
10E18
10E17
10E16
10E15
DEUTERIUM CONCENTRATION (atoms/cm³)
2
4
6
8
10
12
14
16
18
20
DEPTH (μm)

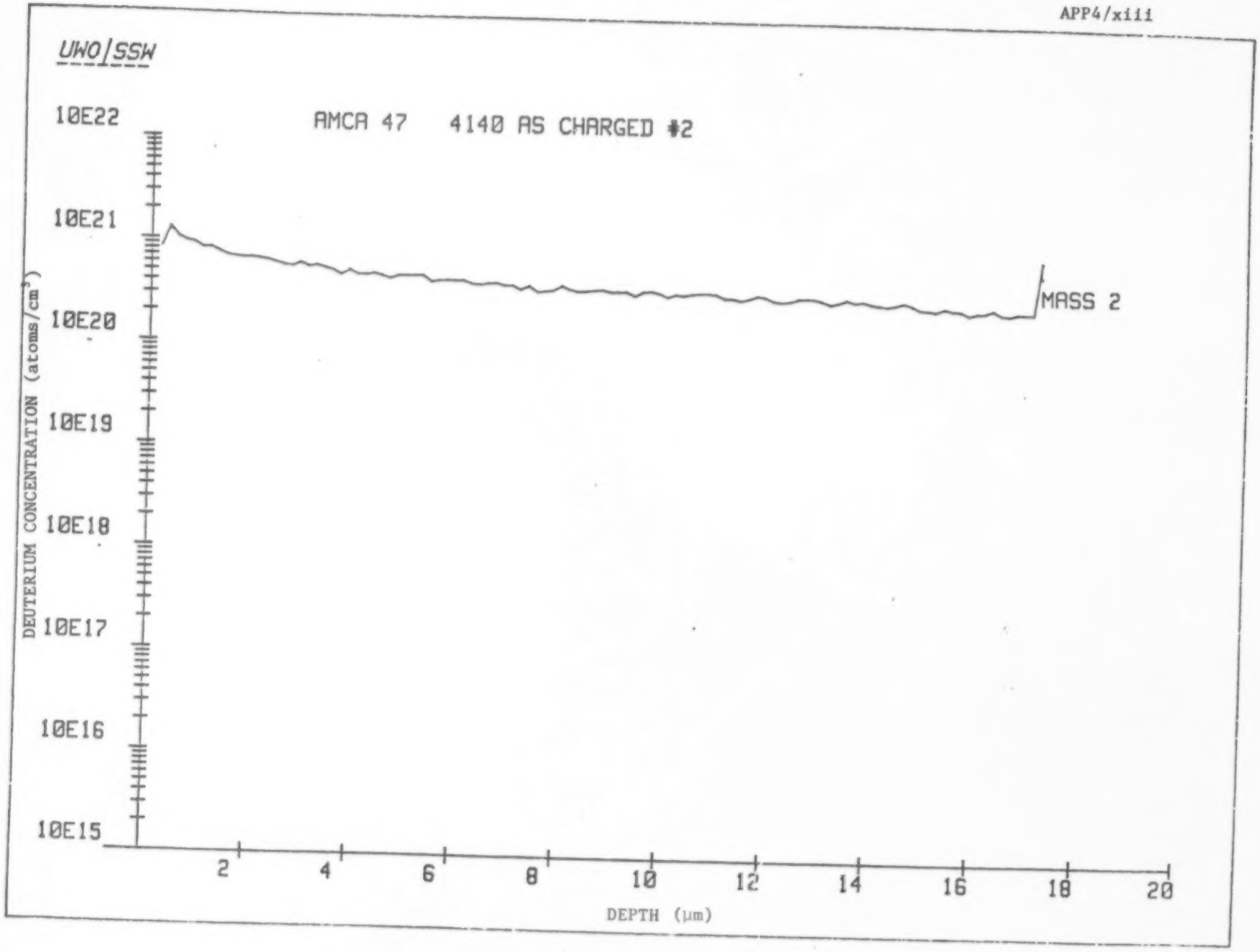

UWO/SSW.
24/4/86
4037 D2 AMCA44
10E22
10E21
10E20
10E19
10E18
10E17
10E16
10E15
DEUTERIUM CONCENTRATION (atoms/cm3)
MASS 2
2
4
6
8
10
12
14
16
18
20
DEPTH (µm)

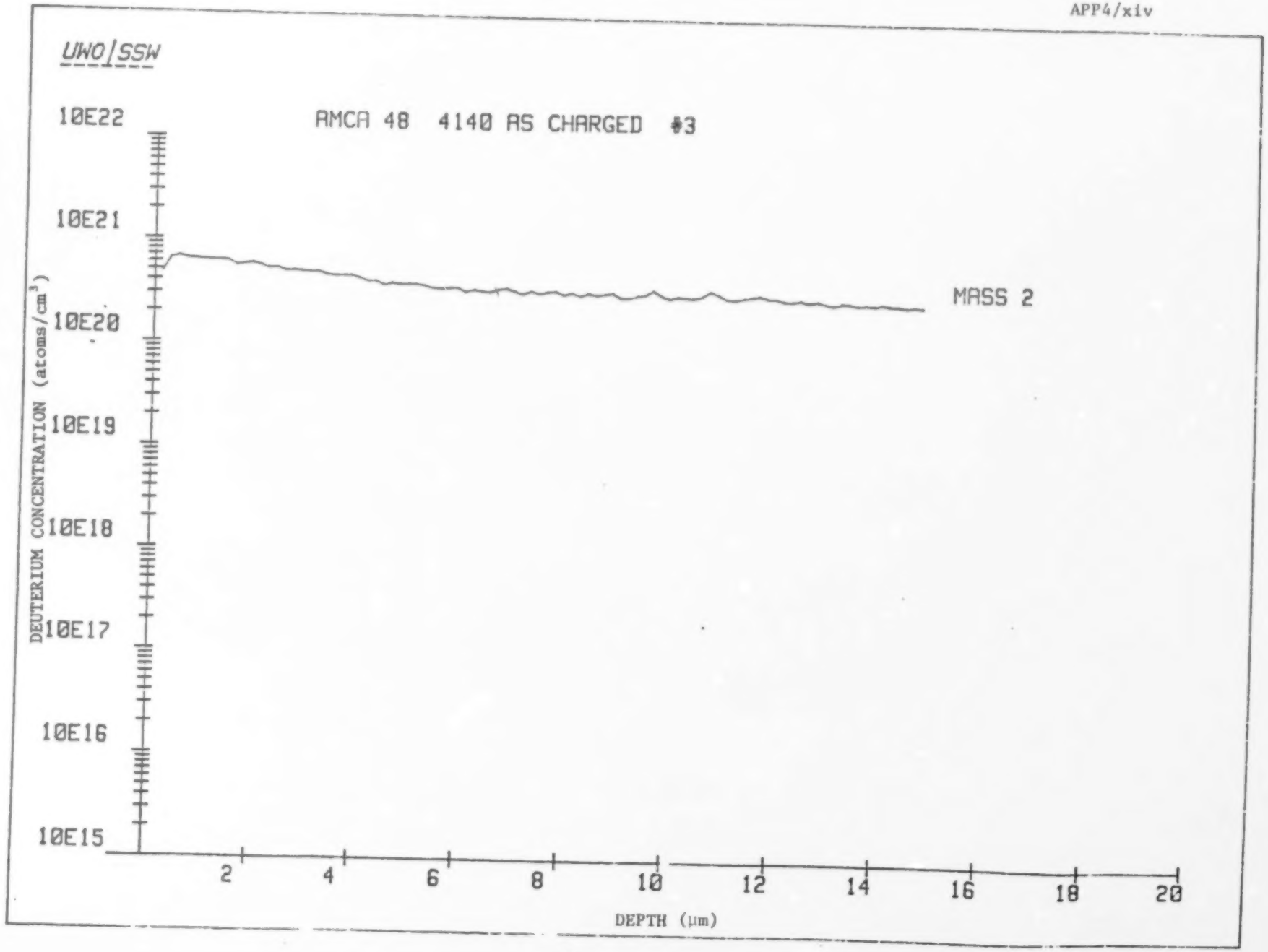

UWO/SSW
24/4/86
AMCA25 4037 D2 NAP 3min
MASS 2
DEUTERIUM CONCENTRATION (atoms/cm³)
10E22
10E21
10E20
10E19
10E18
10E17
10E16
10E15
2
4
6
8
10
12
14
16
18
20
DEPTH (μm)

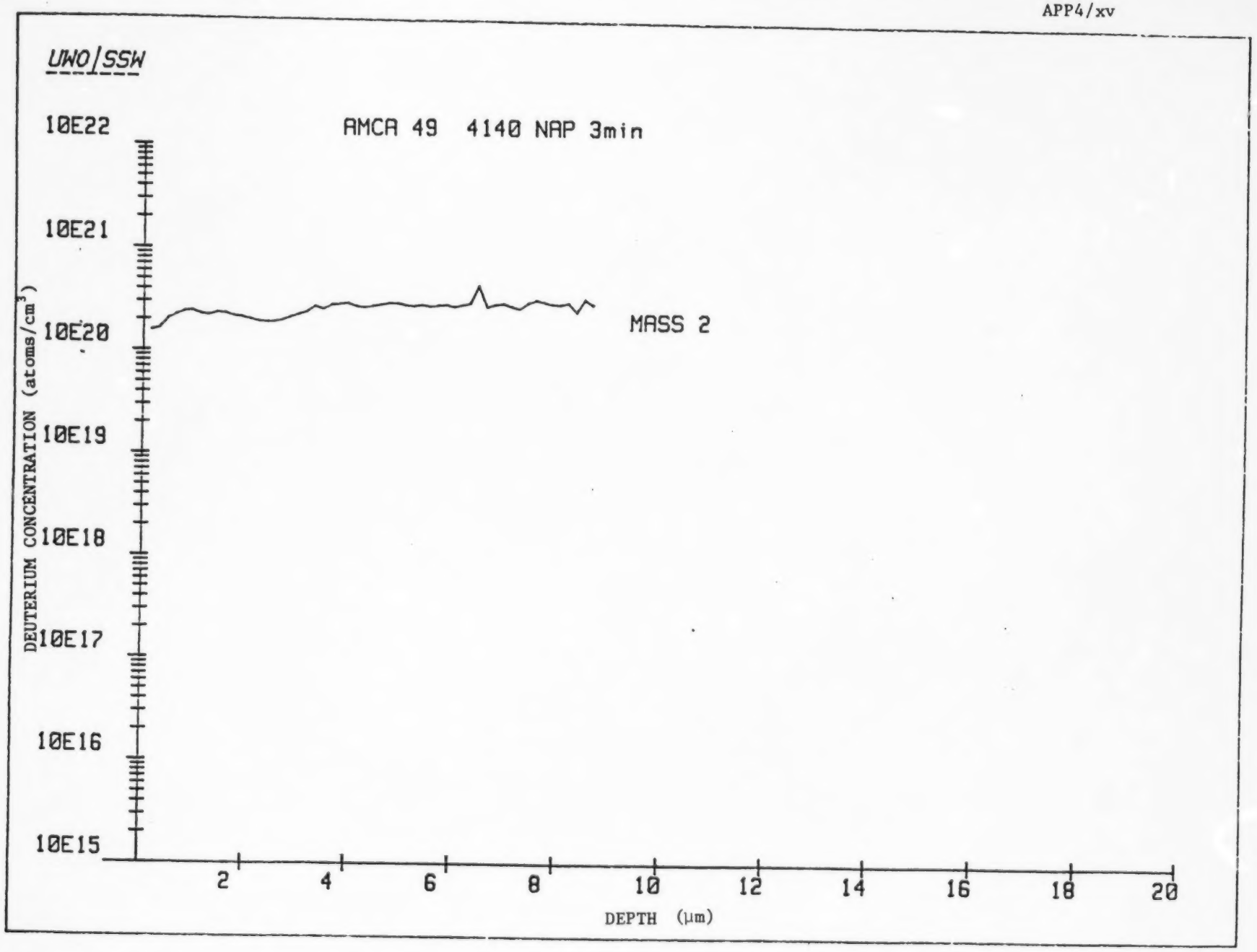

UWO/SSW
24/4/86
AMCA26 4037 D2 NAP 3min
10E22
10E21
10E20
10E19
10E18
10E17
10E16
10E15
DEUTERIUM CONCENTRATION (atoms/cm³)
MASS 2
2
4
6
8
10
12
14
16
18
20
DEPTH (μm)

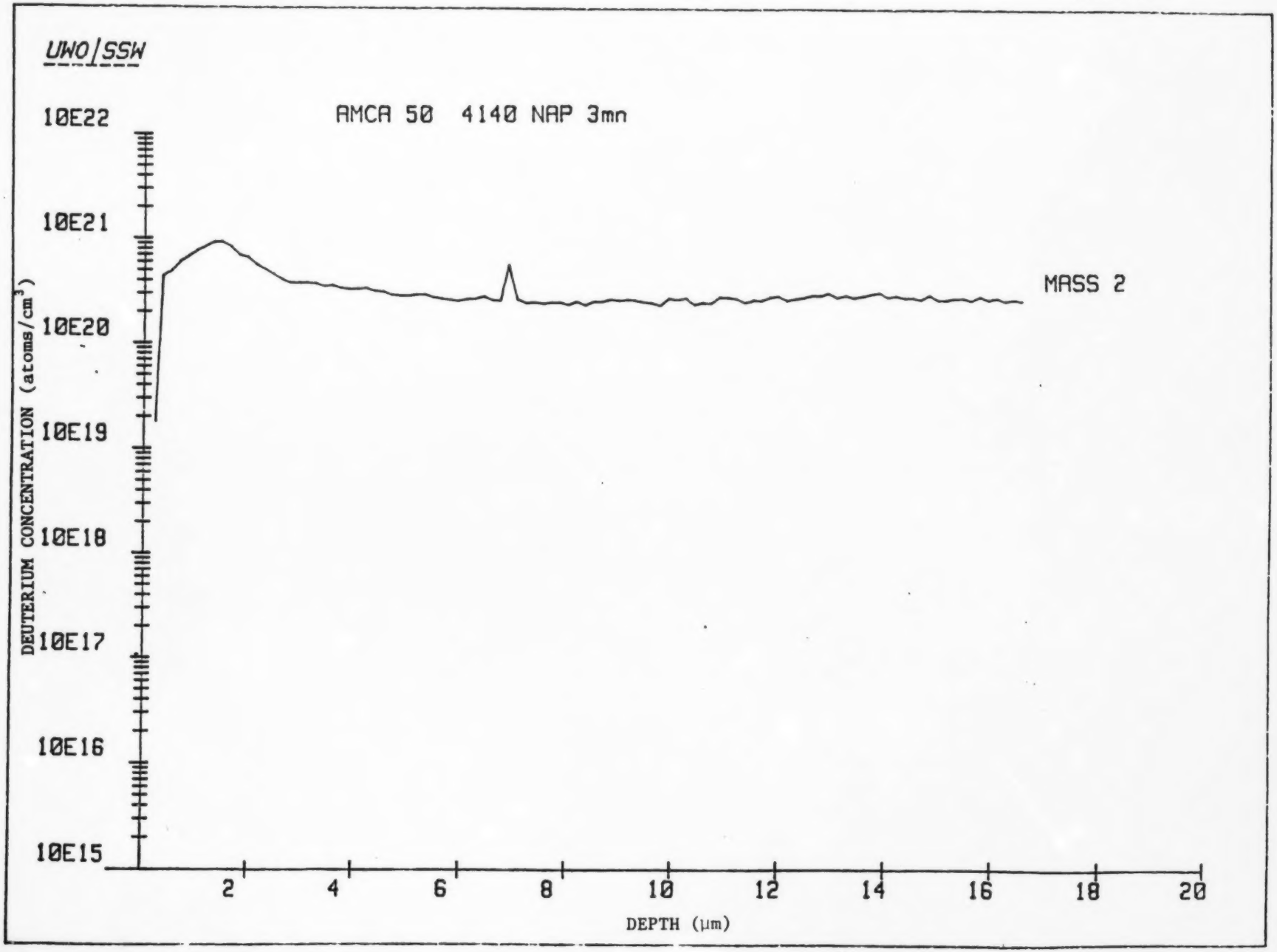

UWO/SSW
24/4/86
AMCA45 4037 D2 NAP
10E22
10E21
10E20
10E19
10E18
10E17
10E16
10E15
DEUTERIUM CONCENTRATION (atoms/cm³)
MASS 2
2
4
6
8
10
12
14
16
18
20
DEPTH (μm)

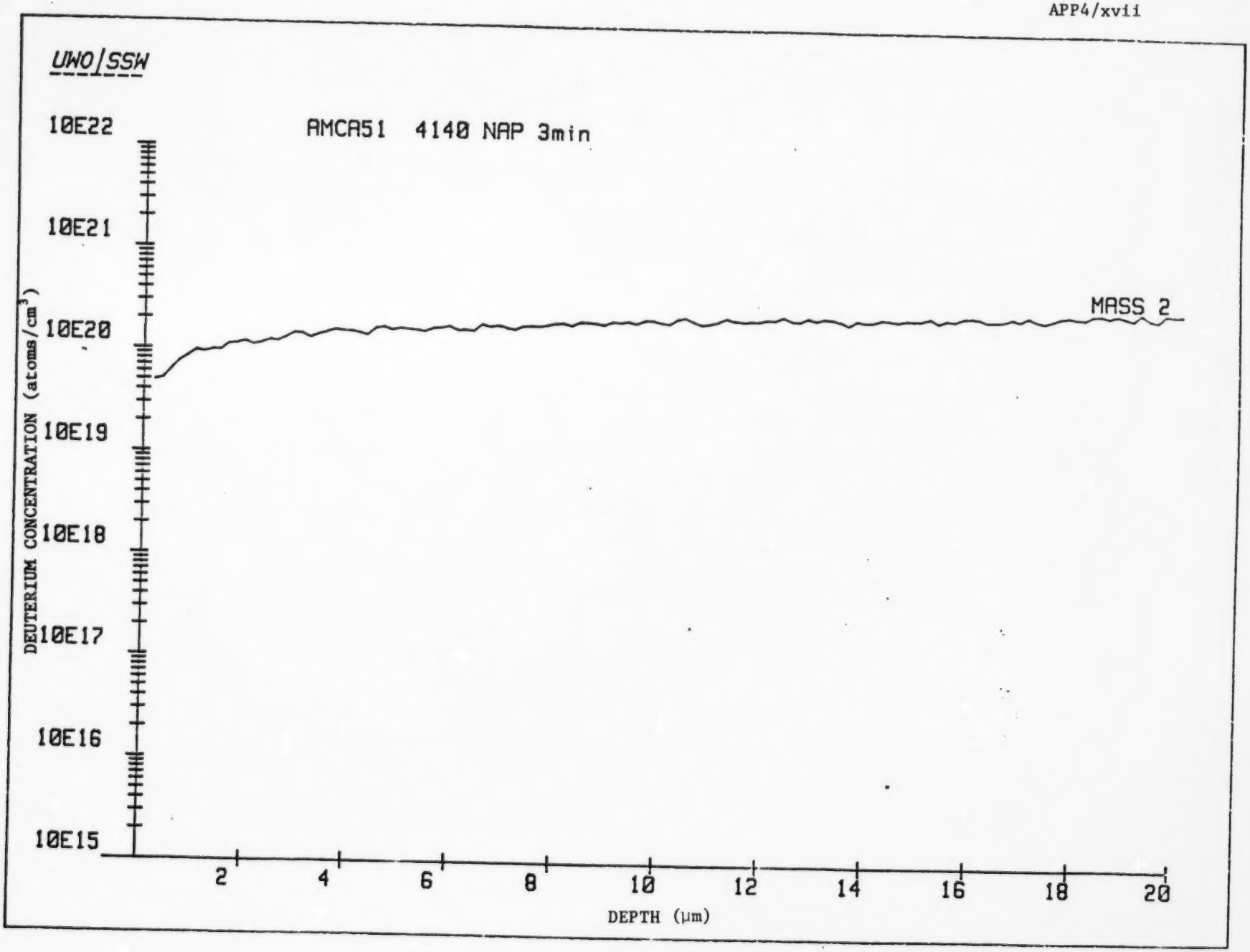

UWO/SSW
AMCA46 4140 AS CHARGED
MASS 2
DEUTERIUM CONCENTRATION (atoms/cm³)
10E22
10E21
10E20
10E19
10E18
10E17
10E16
10E15
2
4
6
8
10
12
14
16
18
20
DEPTH (μm)


UWO/SSW
AMCA 47 4140 AS CHARGED #2
MASS 2
DEUTERIUM CONCENTRATION (atoms/cm³)
10E22
10E21
10E20
10E19
10E18
10E17
10E16
10E15
2
4
6
8
10
12
14
16
18
20
DEPTH (μm)


UWO/SSW
AMCA 48 4140 AS CHARGED #3
MASS 2
DEUTERIUM CONCENTRATION (atoms/cm³)
10E22
10E21
10E20
10E19
10E18
10E17
10E16
10E15
2
4
6
8
10
12
14
16
18
20
DEPTH (μm)


UWO/SSW
AMCA 49 4140 NAP 3min
MASS 2
DEUTERIUM CONCENTRATION (atoms/cm³)
10E22
10E21
10E20
10E19
10E18
10E17
10E16
10E15
2
4
6
8
10
12
14
16
18
20
DEPTH (μm)


UWO/SSW
AMCA 50 4140 NAP 3mn
MASS 2
DEUTERIUM CONCENTRATION (atoms/cm³)
10E22
10E21
10E20
10E19
10E18
10E17
10E16
10E15
2
4
6
8
10
12
14
16
18
20
DEPTH (μm)


UWO/SSW
AMCA51 4140 NAP 3min
MASS 2
DEUTERIUM CONCENTRATION (atoms/cm³)
10E22
10E21
10E20
10E19
10E18
10E17
10E16
10E15
2
4
6
8
10
12
14
16
18
20
DEPTH (μm)